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CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL LABORATORY, HARVARD UNIVERSITY.

WATER, IN THE LIQUID AND FIVE SOLID FORMS, UNDER PRESSURE.

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INTRODUCTION.

THE purpose of this paper is the same as that of the immediately preceding paper on mercury, — to indicate the nature of the fundamental facts which must be taken account of in any theory of liquids valid for high pressures, and to find something about the nature of the equilibrium between crystal and liquid. Both of these subjects are as yet practically untouched. All present theories of liquids are incompetent to explain known facts, and as for the theory of the equilibrium liquid-solid, even the fundamental facts are unknown. It seems, moreover, that these two subjects will find their best development side by side; one involves the other. Thus, any normal liquid may be made to crystallize by the application of high pressure. The internal forces producing crystallization must be present to some extent continuously in the liquid, modifying its behavior more and more as the crystallization point is approached. Yet no present theory of liquids takes account of these vector forces in the liquid which ultimately produce crystallization, but supposes instead that the force between molecules is uniform in every direction.

To be of significance the experimental study must be made over a comparatively wide pressure range, the order of the pressures being many fold greater than the pressures involved in the corresponding study of the liquid-vapor change. The results of this paper reach to 20,500 kgm./cm.^{2}, whereas the highest previous pressure under which water has been studied was only 3500 kgm.

As compared with mercury, the results for water are much more varied and richer in suggestion. It is well known that under ordinary conditions water is abnormal in many respects. The effect of high pressure is to wipe out this abnormality. The manner in which the abnormality disappears with increasing pressure is interesting. Beyond the disappearance of abnormality, the pressure has been pushed far enough to suggest in one or more particulars what the behavior of any liquid must be under very high pressures. The results with mercury did not suggest this so strongly, because the effect of pressure is much less on the properties of mercury than on those of water, so that to produce the effects peculiar to high pressure will require a much higher pressure for mercury than for water. Corresponding to the abnormal behavior of the liquid at low pressures, and probably connected with it, the solid also shows abnormal behavior at low pressures, appearing in no less than five allotropic forms. In addition to these five forms of ice with known regions of stability, there may possibly be two others with no domain of stability whatever. All of these forms, except ordinary ice, are more dense than water. With higher pressures, accompanying the return of the liquid to normality, the tendency of the solid to take new forms apparently disappears, the modification of ice stable at high pressures giving indications of being the last form, corresponding to the completely normal liquid. Here again the last form of ice has been studied over so wide a range as to suggest what may be the effects peculiar to high pressure for the equilibrium between any normal liquid and its solid.

The experimental study of the allotropic forms of ice involves the mapping of their regions of stability, by locating the transition curves, whether to the liquid or to some other solid form, and the measurement on these transition lines of the change of volume and the latent heat of transformation. Five of the six possible stable triple points have been found, and ten of the eleven possible stable transition lines of equilibrium have been followed. The sixth triple point and the eleventh equilibrium line lie at temperatures so low and at pressures so high that the slowness of the reaction makes them practically impossible to determine.

The methods used gave evidence on other points of interest, such as the variation in the reaction velocity with changes of temperature and pressure, the possibility of subcooling or superheating, and the compressibility and dilatation of the solid under pressure.

The data on these different curves are so numerous and bewildering in variety that there is considerable difficulty in choosing the order of presentation. This difficulty is increased by the fact that the paper itself was not planned from the beginning, but has been a growth. The first intention was to measure the isothermal compressibility of water at 0° and room temperature. The existence of a new modification of ice above 0° was not then suspected. When this was discovered in the course of the compressibility measurements, the plan of the paper was extended so as to take in the investigation of this new form of ice over the same temperature range as the compressibility determinations. The compressibility measurements were then completed and the investigation of this new form of ice taken up. This led into all the unsuspected complications of the equilibrium conditions between the five different forms of ice, which necessitated the expenditure of much more time than had been anticipated. It then became necessary, for the sake of completeness, to measure the compressibility of water in its region of existence as a liquid below 0°. During this work with the various modifications of ice, experimental familiarity with the possibilities of high pressure apparatus had been increasing, so that it became possible to extend the work on the ice first found to nearly twice the pressure range reached in the compressibility measurements. This is the state of the work as presented here. To be complete, the compressibility of water should now be redetermined over an increased temperature range corresponding to the increased pressure range, but this process of advancement might be continued indefinitely and a stop has to be made somewhere. For instance, it would probably be possible with the means now at hand to measure directly the compressibility and the dilatation of these various forms of ice, and also the adiabatic compressibility of the liquid. As it is, the pressures have been pushed far enough on both the liquid and the solid to indicate what the general nature of the effects for the highest pressures may be. The pressure required to indicate this is higher for the solid than for the liquid, so that the lack of complete parallelism between the results for the liquid and the solid is partly justified.

The order of presentation finally chosen arranges the subject matter in two parts. The first deals with the compressibility of the liquid at different temperatures. The second, by far the longer, gives the data for the different modifications of the solid, including the quantities involved in the transition solid-solid as well as in the transition solid-liquid. The order of presentation in the second part will be the natural order, proceeding systematically from the lower to the higher pressures.

This systematic order was not, as has been stated, the actual order of the experiment. The existence of another form of ice stable at high pressures and at temperatures above zero was first discovered by the anomalous results of the compressibility determinations. The existence of this form was then made certain by the measurement of the electrolytic conductivity of very dilute solutions, there being a change in the conductivity when the transition occurs. Not until then was the present method adopted by which the equilibrium pressure and change of volume were measured simultaneously, but even with this new method the curve was followed down, from high temperatures and pressures to lower temperatures and pressures. The domain of temperatures and pressures in which Tammann worked (up to 3500 kgm.) was approached with the distinct prejudice, therefore, that Tammann's work was incorrect, because there seemed no possible connection between the curves given by Tammann and the curves at the higher pressures. This prejudice makes more valuable, therefore, the essential verification of Tammann's work found at the low pressures. The expected discrepancy was avoided by the remarkable versatility of ice in appearing in different forms.

The experimental methods are in large part the same as those used in the preceding paper on mercury. Reference is made to that paper for detailed discussion. Where new methods have been necessary, discussion is given here in the appropriate place.

In presenting the data, the aim has been to give enough so that any one could, if he wished, check the computations for himself. Every one of the original observations, except those marred by obvious accidents, has been given. The table of contents should, however, enable one to omit the generally uninteresting discussion of details of methods and critical examination of data, and proceed to the discussion of the general results. In connection with the equilibrium of the different solid forms, it is suggested that some may find it clearer to read first the short history of the experiment, the description of the general nature of the experimental methods, and the description of the manner of appearance of the new forms of ice given first under the heading "The curve VI–L," and then under "The curve V–L."

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The Compressibility of Water.

A complete thermodynamic knowledge of any substance over any range of temperature and pressure is afforded by a knowledge of the characteristic equation of the substance over that range (that is, the relation connecting volume with temperature and pressure), and a knowledge of the specific heat along some curve of the pressure-temperature plane not an isothermal. For water, the specific heat is known in its dependence on temperature at atmospheric pressure, that is, along a line not an isothermal, so that theoretically all that is needed for a complete thermodynamic knowledge of water is the knowledge of the characteristic equation. This knowledge is evidently given by the change of volume with pressure along various isothermals, together with the change of volume along some line not an isothermal. Practically this means that the characteristic equation may be found by finding the isothermal compressibility at several different temperatures and combining with the known dilatation at atmospheric pressure.

It does not follow, however, that all the thermodynamic data are given with equal accuracy by the knowledge of these quantities. Thus the specific heat, which involves a second derivative of the p-v-t relation, can evidently be found much less accurately than the compressibility, for example. Therefore, while some hold is obtained by the data of this paper on all the thermodynamic quantities, some of these will be found more accurate than others.

Two methods were used in determining the compressibility. The first is the same as that used in determining the compressibility of mercury, and has already been fully described and critically discussed in the previous paper. Briefly, it consists in enclosing the water to be measured in a steel bottle, communicating at the upper end through a very fine channel with a mercury reservoir. The bottle and the reservoir are completely immersed in a fluid to which pressure is applied. The water contracts under pressure, mercury from the reservoir runs in to take its place, falls to the bottom of the bottle, and is weighed after pressure is removed. Compressibility was measured by this method at two temperatures, 0° and 22°, and the same method evidently might be used at any temperature above zero. Under pressure, however, water may exist as the liquid at temperatures considerably below zero, so that for a complete knowledge of the p-v-t surface of water, the volume must be measured throughout this extended region. The method just described is evidently not applicable here without a troublesome variation of both temperature and pressure together during a single measurement, and a second method was adopted.

The second method, which was used to obtain the changes of volume below zero, assumes as correct the compressibility at zero as found by the first method. The data given by this second method are the thermal dilatation from zero at constant pressure for a number of different pressures. Combined with the known volume at zero, this is evidently sufficient to give the volume at any temperature and pressure.

The apparatus used was the same as that already described in determining the data on the freezing curve of mercury, and consists of a lower cylinder placed in a thermostat, and an upper cylinder in which the pressure is produced by a moving piston. The water under experiment is placed in a cylindrical steel shell in the lower cylinder. The lower cylinder also contains the manganin resistance coil with which pressure is measured. The measurements of pressure by this method have been described in a previous paper. The remainder of the lower cylinder and the entire upper cylinder is filled with gasolene, by which pressure is transmitted to the water.

The experimental procedure was as follows. The temperature of the lower cylinder was maintained at some value below zero by the thermostat, and the pressure varied over the region of existence of water for this temperature. The piston displacement was plotted as a function of the pressure for this temperature. The temperature of the thermostat was then raised by a suitable amount, and the piston displacement found as a function of the pressure for this new temperature. This was done for four different temperatures, including zero. From these four curves, with the help of an interpolation for temperature, the piston displacement may be found for any temperature and pressure in the region of the liquid water below zero. This displacement was found at 5° intervals for several different pressures, increasing in steps of 800 kgm. At each pressure, therefore, the thermal dilatation may be found by taking the difference between the displacement at the desired temperature and zero.

If the experiment were performed in the simple manner described, evidently several very serious errors would be introduced. No account whatever has been taken of the thermal dilatation of the steel cylinder, which is not very large, or of the gasolene transmitting the pressure, which is comparatively more important. These two disturbing effects were corrected for by two auxiliary experiments. In the first, the lower cylinder was almost entirely filled with a cylinder of bessemer steel, and the displacement found for any temperature and pressure of the region in question, exactly as for water. In the second auxiliary experiment, the lower cylinder was entirely filled with gasolene, and the displacement found as before. In applying the correction, the entire interior of the apparatus may be thought of as consisting of two parts; one portion is that which would be occupied by the bessemer cylinder, and the second portion is all the rest, including the remainder of the lower cylinder and the upper cylinder. It is to be noticed that this "first part of the volume" is purely fictive: it need not be actually occupied by the bessemer. In the auxiliary experiment in which the lower cylinder is filled with gasolene, this "first part of the volume" is filled with gasolene; in the actual experiment with water, the "first part of the volume" is filled partly with the steel of the shell, partly with water, and partly with enough gasolene to make up the difference. The advantage in thus thinking of the volume as split up into two parts is that the second part remains the same in the three experiments. The displacement of the piston at constant pressure due to change of temperature of the thermostat will evidently include, for "the second part," the thermal dilatation of the cylinder, and what is important, will be independent of the position of the piston in the upper cylinder, since only the lower cylinder is involved in the change of temperature. By taking the difference of the apparent dilatations at constant pressure for the three experiments we shall obtain, therefore, two differences, from which the effect of the "second part of the volume" has been eliminated. These two differences involve the change of volume with temperature at constant pressure of the material occupying the same volume that the bessemer steel would have under the same conditions of temperature and pressure. The quantities entering into the two differences are, therefore, the thermal dilatation of bessemer steel, of gasolene, and of water at various pressures. Now the thermal dilatation of bessemer steel is very small comparatively, and is furthermore known to be little affected by changes of pressure. For the accuracy required in this work, therefore, the change of volume of the steel cylinder, both with temperature and pressure, may be assumed to be known. This leaves only two unknown quantities in the two differences mentioned above, so that either may be found. The thermal dilatation of the gasolene is found immediately from the difference of the displacements of the two auxiliary experiments. It should be noticed that the dilatation is used here in a sense slightly different from the usual one in thermodynamics. The quantity given here is the change in volume in cm.^{3} for 1° lowering of the temperature of the quantity of gasolene which at that pressure occupies 1 cm.^{3}. To find the change of volume of the quantity of gasolene which originally at 0° and atmospheric pressure occupied 1 cm.^{3} we should need to know in addition the compressibility of the gasolene. It is an advantage of the method that it is not necessary to know this compressibility. It is now obvious why a knowledge of the compressibility of water at 0° is necessary. The quantity of water is fixed. As the pressure is raised, the part of the "first part of the volume" occupied by the water decreases in a way known, because the compressibility is known, and the part occupied by the gasolene correspondingly increases. At any pressure, therefore, the number of cm.^{3} of gasolene concerned in the total dilatation of the "first part of the volume" is known, the dilatation per cm.^{3}, and so the total dilatation of the gasolene is also known, and therefore the remainder of the total dilatation due to the water is given immediately.

There are several minor corrections to be considered. The change of volume as given in cm.^{3} by the displacement of the piston involves directly the diameter of the piston. This changes with pressure. This correction has been already discussed in the mercury paper and found to be 1.35 per cent for 10,000 kgm. The magnitude is almost negligible for the present work, but the correction was nevertheless applied in making the computations. Furthermore, the volume swept out by the piston at constant pressure during a change of temperature of the lower cylinder does not represent accurately the change of volume of the material of the lower cylinder. This is due to the fact that the upper cylinder was kept at the constant temperature of 8° instead of 0°. For example, let us suppose that the contents of the lower cylinder expand 1 per cent when the temperature is raised from — 20° to 0°. This 1 per cent passes from the lower cylinder at 0° to the upper cylinder at 8°, and in so doing experiences an additional increase of volume due to the extra 8°. The error introduced by assuming the piston displacement to give the dilatation will be, therefore, in this example, about 0.5 per cent on the dilatation. This error was not corrected for in the present work, since the accuracy of the largest dilatation found, judging only from the number of significant figures, was not over 2 per cent.

One experimental source of error did require correction. This is due to the wearing away of the packing material of the piston by the enormous friction during the advance of the piston. The effect is evidently the same in its results as a leak, although there was absolutely no leak of the liquid and only this wearing away of the packing during actual motion of the piston. The effect was corrected for by making two runs at every temperature with increasing and decreasing pressure, and taking the mean. The discrepancy between the displacements during increasing and decreasing pressure gave the amount of wearing of the packing. This was of the order of 0.01 inch on a total stroke 3 inches. The maximum correction was 0.013 inch. This correction was applied to the next run at higher temperature. The correction so determined incidentally covers the effect of hysteresis, elastic after-working, or of viscous yield in the steel, all of which must be very small at these comparatively low pressures.

The method used in making the calculations from the data was a combination of arithmetic computation with graphical representation. The graphical representation alone would not have been accurate enough. This is because the changes of volume due to temperature are very small in comparison with those due to changes of pressure in the region in question, so that it was necessary to retain all the significant figures given by the measurements. Piston displacement was measured to 0.0001 inch on a total of 3 inches, but since the pressure measurements were sensitive to only 1 part in 3000, the displacement readings were retained only to 0.001 inch. The method was to pass the best parabola through the experimental points at the various constant temperatures; calculate the displacement given by the parabola at the pressure of the experiment; plot on an enlarged scale the difference between the observed displacement and the calculated displacement; pass a smooth curve through these difference points; and finally by combining the results given by the smooth deviation curve with the computed values on the parabola, to find the displacements at equal pressure intervals. This has the advantage of giving a curve perfectly smooth to the last of the significant figures. Curves thus obtained for the different temperatures were then combined by plotting the displacement corresponding to the same constant pressure against the temperatures of the different curves, and smooth curves were drawn through these points. This last step could be made entirely graphically, since the change of displacement with temperature at constant pressure is comparatively slight. From these two sets of smooth curves, the displacement for uniform pressure intervals of 800 kgm. and uniform temperature intervals of 5° was found over the entire region. These points were found in this way for each of the three experiments, that with water and the two auxiliary ones, and the difference of displacement at corresponding pressures and temperatures combined in the way already described.

The actual data above and below 0° follow. All the details of the calculation of the compressibility at 0° and 22° by the first method were the same as that used for determining the compressibility of mercury. In fact, the two determinations, compressibility of water and compressibility of mercury, were made at the same time and each involves the other. It is to be noticed that the various disturbing factors due to irregularities in the behavior of the steel bottle are much less important in the case of water than they were in the case of mercury. This is because of the higher compressibility of water as compared with that of the mercury. Nevertheless, the effect of these irregularities was distinctly felt here also, particularly if the pressure had been allowed to reach so high a value as to freeze the water. The best results were obtained with piezometers in which the water had never been allowed to freeze.

At 0°, four different piezometers were used, one before and after annealing, so that there are really five independent sets of determinations. Three independent points with a sixth piezometer, No. 1, were also found, but were not used in the computations, because this was the very first trial ever made of the method, and the piezometer had been badly strained by a pressure considerably beyond the freezing pressure, the existence of which was not then suspected. The actual data are given in Table I. To afford a comparison of the regularity of these results as against the values obtained for mercury, the actual points for the second best piezometer, No. 6, are shown plotted in Figure 1. If comparison be made with the mercury points it will be seen that these of Figure 1 are distinctly better. The changes of volume at even pressure intervals, obtained from smooth curves from the data of each of the five piezometers, is shown in Table II., together with the weighted means. Finally, the deviation of the weighted mean from a parabolic formula is plotted against pressure, and a smooth deviation curve drawn. In only two instances does the smooth deviation curve fail to pass through the points of the weighted mean. The value given by this smooth deviation curve is to be taken as the final value, and is also given in Table II. The change of volume is to

TABLE I.

Data for Compressibility of Water at 0°.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$\frac{\Delta v}{v_0}$.
Piez. No. 6.		Piez. No. 7.		Piez. No. 3.		Piez. No. 5′.	
2190	0.0795	2190	.0831	5270	0.1467	6810	0.1589
2970	0979	2970	0993	4520	1348	6090	1505
3740	1137	3740	1139	3750	1184	6810	1603
4500	1282	4500	1289	3000	1012	6800	1618
5270	1412	5270	1417	2220	0832	6070	1523
6020	1496	6020	1528	1450	0590	5340	1412
6760	1618	6760	1626	6050	1552	4540	1270
7110	1657	7110	1666	6770	1651	3770	1116
1420	0595	2960	0981	1000	0423	3020	1003
2180	0796	3740	1152	500	0221	2230	0806
2960	0995	6570	1636	Piez. No. 5.		1440	0564
3740	1152	6750	1605	1410	0.0568	1050	0421
6570	1624	6010	1524	2180	0776	1830	0667
6750	1629	5260	1416	3090	0989	2610	0919
6010	1547	4490	1290	3740	1265	3400	1052
5260	1429	3740	1139	4500	1265	4140	1208
4490	1301	2950	0978	5290	1391	4910	1366
3740	1151	2200	0786	5270	1365	5680	1457
2950	0985	1410	0547	6030	1457	Piez. No. 1.	
2200	0797	1000	0412	6760	1578	6750	0.1710
1410	0561	500	0227	7500		6050	1501
1000	0420					5260	1408
500	0226						

be found at every pressure by combining with the change of volume calculated by the formula

$$\Delta v = ap + bp^2,$$

where $\log a = 5.5942 - 10,$

and $\log(-b) = 1.3512 - 10,$

the small correction term given by the deviation curve of Figure 2.

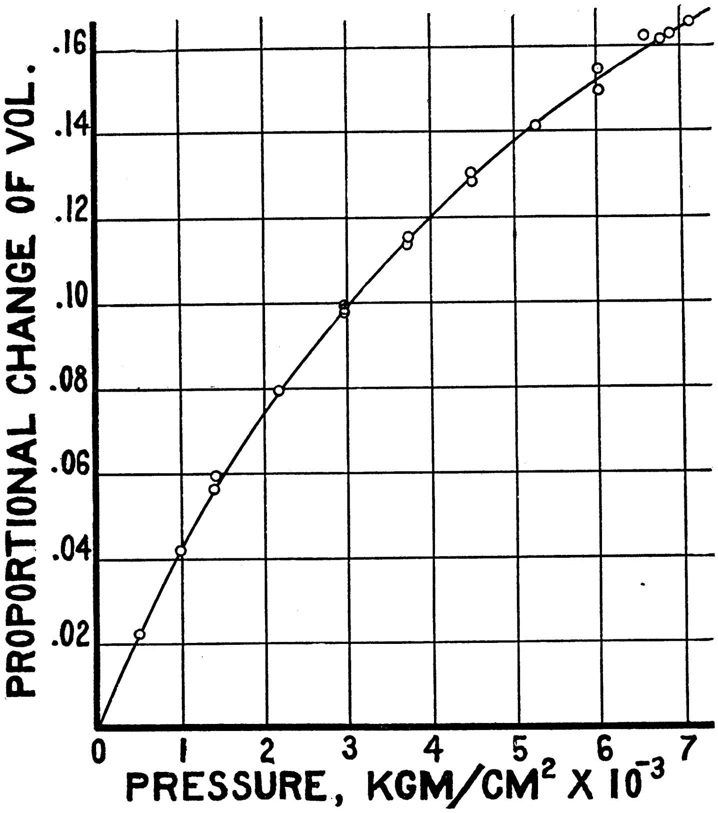

FIGURE 1. The change of volume of water at 0° C. as obtained with piezometer No. 6.

The data for 22° were obtained in exactly the same way. Only three piezometers were used here instead of five as at 0°. The results are slightly less irregular, owing to greater familiarity with the method and greater care exercised to keep the maximum pressure below the freezing pressure. The data are given in Table III.; the smoothed values for each piezometer, the weighted means, and the final values in Table IV. The change of volume at any pressure is to be found by combining with the value given by the formula

TABLE II.

COMPRESSIBILITY OF WATER AT 0°. COMPARISON OF BEST RESULTS WITH DIFFERENT PIEZOMETERS, WEIGHTED MEAN, AND FINAL VALUES.

Pressure, kgm./cm.^{2}.	$\frac{\Delta v}{v_0}$.						
	No. 6.	No. 7.	No. 3.	No. 5.	No. 5′.	Weighted Mean.	Final Value.
500	0.0228	0.0222	0.0230	0.0230	0.0218	0.0224	0.0224
1000	0416	0408	0429	0409	0414	0414	0414
1500	0597	0586	0615	0605	0589	0593	0593
2000	0742	0721	0762	0736	0732	0732	0735
2500	0879	0859	0904	0860	0866	0869	0869
3000	0997	0992	1030	0967	0977	0994	0991
3500	1095	1099	1142	1068	1072	1097	1097
4000	1192	1193	1246	1168	1174	1195	1195
4500	1286	1288	1339	1253	1261	1287	1287
5000	1374	1375	1419	1333	1359	1374	1374
5500	1453	1454	1490	1407	1438	1452	1452
6000	1524	1523	1551	1474	1509	1520	1520
6500	1591	1589	1600	1541	1569	1586	1586
7000	1659	1652	1640	1600	1622	1644	1644
....	.6	1.7	.4	.3	.4	Weight	....

$$\Delta v = ap + bp^2,$$

where $\log a = 5.5139 - 10,$

and $\log(-b) = 1.1239 - 10,$

the correction given by the deviation curve of Figure 3. It is to be noticed that both of these formulas, for 0° and 22°, take as the unit of volume the volume which the given quantity of water occupies under unit pressure at 0° or 22° respectively. To find the change of volume of 1 gm. of water, a correction must be applied for thermal dilatation between 0° and 22°.

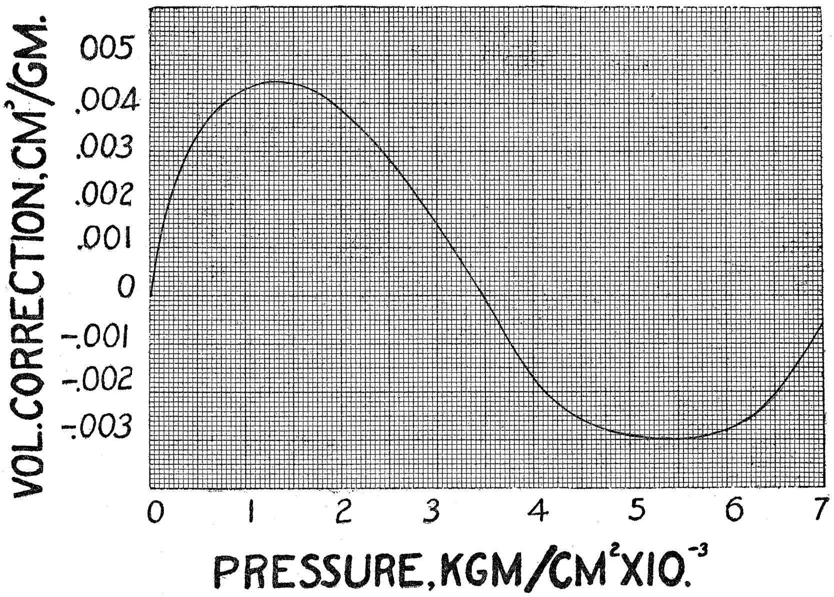

FIGURE 2. The deviation curve for water at 0°. This is to be used in combination with the formula on page 453 in determining the change of volume at 0° C.

These data may be compared with those of Amagat[1] (Table V.). In making this comparison, it must be borne in mind that this is a disproportionally severe test of these data. Values taken from the low end of a large range cannot be expected to show as small a percentage of error as will values obtained with apparatus designed only for this smaller range. In the present work very few actual experimental points were found below 1000 kgm.; the lower end of the curve is virtually an extrapolation to a known zero. The values of the present work are, with only one exception, lower than those of Amagat. The absolute value of the discrepancy becomes less at the higher pressures, as it should, since the comparison with the present values is made under more favorable conditions at the higher pressures. The fact that the absolute value of the discrepancy tends to become less, not greater, shows that the fundamental unit of pressure must be essentially the

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[1] Amagat, Ann. de Chim. et Phys. (6), **29**, 68–136, 505–574 (1893).

TABLE III.

Data for Compressibility of H_2O at 22°.

Pressure, kgm./cm.^{2}.	$\frac{\Delta v}{v_0}$.	Pressure, kgm./cm.^{2}.	$\frac{\Delta v}{v_0}$.
Piez. No. 6.		Piez. No. 7.	
1460	0.0522	1460	0.0537
2660	0853	2660	0836
3790	1101	3790	1060
4950	1288	4950	1311
6120	1470	6120	1470
7180	1615	7180	1614
8290	1732	8290	1730
		Piez. No. 9.	
3220	0981	3220	0.0978
2170	0732	2170	0730
4350	1206	4350	1202
9530	1889	9530	1999
10930	2041	10930	2046
12250	2619	12250	2612
5700	1458	5700	1469
6740	1571	6740	1612
7830	1706	7830	1754
495	0203	495	0204
995	0391	995	0403
6170	1493	6170	1488
8960	1839	8960	1832
10340	2394	10340	1983
11570	2634	11570	2147

same for the two determinations. Furthermore, the dilatation between 0° and 22°, as found by taking the difference of the compressions at 0° and 22°, is evidently going to show much less absolute difference for the two sets of determinations than the compressibilities, suggesting that the two sets are each consistent with themselves, since they show the same temperature effect.

TABLE IV.

Compressibility of H_2O at 22°. Comparison of Best Results with Different Piezometers, Weighted Mean, and Final Values.

Pressure, kgm./cm.^{2}.	$\frac{\Delta v}{v_0}$.				
	No. 6.	No. 7.	No. 9.	Weighted Mean.	Final Value.
1000	0.0383	0.0379	0.0391	0.0383	0.0383
2000	0683	0667	0684	0679	0679
3000	0933	0914	0933	0928	0928
4000	1141	1123	1145	1137	1137
5000	1316	1304	1324	1314	1314
6000	1462	1460	1485	1465	1465
7000	1595	1594	1631	1600	1600
8000	1723	1702	1761	1728	1728
9000	1850		1885	1855	1855
10000	1963		2000	1967	1967
11000	2036		2078	2042	2042
	4	2	1	Weight.	

Since this paper was written, Parsons and Cook[2] have published data for the compressibility of a few liquids up to 4500 atmos. Their results for water at 4° are shown in Table V*a*. compared with the results of this paper. The agreement is closer than 1 per cent at the higher pressures. The results of Parsons and Cook differ from those of Amagat in the same direction as those found here and by about twice as much. The values given in the table as the result of the present work were calculated from the data of Table XXXI. on page 539.

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[2] Parsons and Cook, Proc. Roy. Soc. A, **85**, 332–349 (1911).

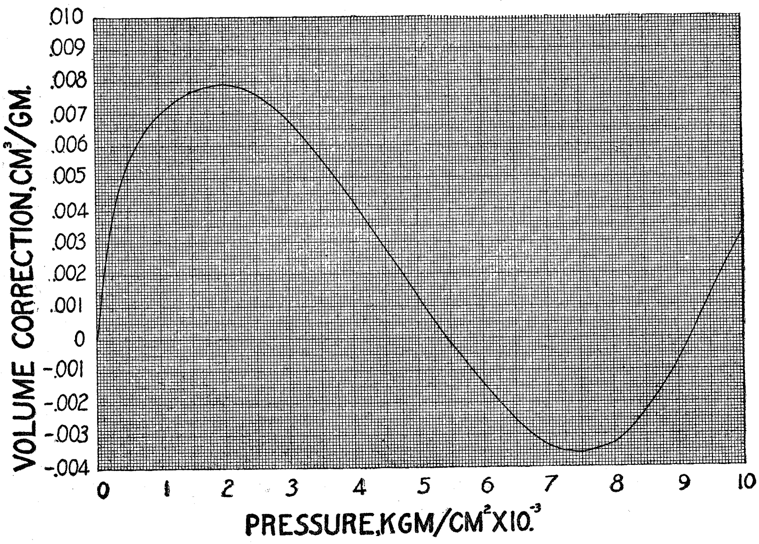

FIGURE 3. The deviation curve for water at 22°. This is to be used in combination with the formula on page 454 in determining the change of volume at 22°.

The results obtained by the second method below 0° next concern us. To give the original data would occupy so much space as to be out of the question. The methods and the details of the calculation have already been described. It is sufficient to give here some information about the actual data, and the probable accuracy. Four runs were made with water, at –15°.8, –10°.2, –5°.0, and 0°.0, and displacement and pressure measured at respectively 8, 10, 14, and 17 points. Each of these pressure measurements was the mean of two readings, and the displacement measurements the mean of four. The auxiliary experiment with the lower cylinder full of bessemer was also made at four temperatures: –17°.7, –12°.2, –6°.0, and 0°.0, and the number of points at these temperatures was 14, 15, 13, and 16 respectively. The auxiliary experiment with the lower cylinder full of gaso-

TABLE V.

Comparison of Results for Compressibility of Water with those of Amagat.

Pressure.		Δv.					
		At 0°.			At 22°.		
Atmos.	$\frac{\text{kgm.}}{\text{cm.}^2}$.	Amagat.	This Work.	δ.	Amagat.	This Work.	δ.
500	516	0.0237	0.0231	− 6	0.0216	0.0220	+ 4
1000	1033	0440	0425	−15	0402	0394	− 8
1500	1549	0611	0599	−12	0565	0552	−13
2000	2066	0763	0753	−10	0710	0697	−13
2500	2583	0898	0891	− 7	0839	0829	−10
3000	3099	1017	1013	− 4	0957	0950	− 7

TABLE V*a*.

Pressure.		ΔV at 4°.	
Atmospheres.	kgm./cm.^{2}.	Parsons and Cook.	This Work.
0	0	0.000	0.0000
500	516	0.022	0.0226
1000	1033	0.042	0.0418
1500	1549	0.059	0.0591
2000	2066	0.073	0.0742
2500	2583	0.086	0.0879
3000	3099	0.098	0.1002
3500	3615	0.109	0.1103
4000	4132	0.120	0.1203
4500	4648	0.130	0.1306

TABLE VI.

DILATATION OF WATER BELOW 0° — DISPLACEMENT OF PISTON AT REGULAR INTERVALS OF PRESSURE AND TEMPERATURE.

Pressure.		Piston Displacement, inches.				
Slider Displacement, cm.	$\frac{\text{kgm.}}{\text{cm.}^2}$.	−20°.	−15°.	−10°.	−5°.	0°.
		Lower cylinder full of water.				
3	800	....	0.642	0.636	0.627	0.623
6	1600	....	1.137	1.133	1.125	1.112
9	2400	1.542	1.533	1.521	1.508	1.483
12	3200	1.861	1.848	1.834	1.818	1.797
15	4000	2.126	2.118	2.108	2.093	2.073
18	4800	....	2.342	2.339	2.332	2.307
21	5600	....	....	....	2.544	2.521
24	6400	....	....	....	....	2.718
		Lower cylinder full of bessemer.				
3	800	0.427	0.423	0.419	0.415	0.411
6	1600	0.721	0.717	0.712	0.706	0.697
9	2400	0.936	0.932	0.927	0.920	0.912
12	3200	1.112	1.110	1.105	1.098	1.089
15	4000	1.268	1.265	1.262	1.257	1.251
18	4800	....	1.402	1.398	1.393	1.387
21	5600	....	....	1.524	1.520	1.516
24	6400	....	....	....	....	1.629
		Lower cylinder full of gasolene.				
3	800	0.904	0.884	0.855	0.818	0.762
6	1600	1.494	1.470	1.442	1.411	1.378
9	2400	1.916	1.893	1.867	1.838	1.805
12	3200	2.276	2.256	2.228	2.203	2.176
15	4000	2.554	2.538	2.520	2.499	2.473
18	4800	2.815	2.797	2.778	2.756	2.733
21	5600	3.036	3.023	3.008	2.991	2.971
24	6400	....	....	....	....	3.177

lene was made at only three temperatures: −15°.2, −7°.1, and 0°.0, with 16, 16, 16 points respectively. All of these points, with very few exceptions, lay on smooth curves consistently to 0.001 inch.

The results of the graphical computations of displacement and pressure at equispaced points are shown in Table VI. The displacement at zero pressure is arbitrary in these tables. The data of these tables, together with the quantities of steel, water, and gasolene, are sufficient to enable anyone to check up the computations. The weight of the steel cylinder filling the lower cylinder was 286.345 gm. The weight of the steel shell containing the water was 51.818 gm. The weight of the water was 26.775 gm. The density of steel was 7.840 at 17°, and it was assumed that the cubical dilatation of steel was 0.00036 and the cubical compressibility $0.0_6 6$ in kgm./cm.². The volume in cm.³ of the bore of the upper cylinder, 1 inch long, was 4.117 cm.³. With increasing pressure this increases 1.35 per cent for 10,000 kgm.

TABLE VII.

Dilatation of Water below 0° at Various Pressures.

Pressure, kgm./cm.².	Change of Volume in cm.³ per gm. on changing from Tabulated Temperature to 0°.				
	−20°.	−15°.	−10°.	−5°.	0°.
			−0.00173	−0.00057	0
800		−0.00015	00031	00062	0
1600	0.0000	0000	0000	0000	0
2400	0045	0038	0028	0017	0
3200	0052	0043	0029	0017	0
4000	0045	0040	0031	0017	0
4800		0034	0033	0022	0
5600				0023	0

The results of the computations from the data of these tables are given in Table VII. and Figure 4, showing the proportional change of the original volume at 0° and atmospheric pressure by which the water shrinks at various pressures on passing from 0° to the temperature listed.

From these results, both above and below 0°, the actual volume of the water for regular pressure and temperature intervals has been found and is given in Table XXXI. on page 539.

THE SOLID PHASES OF WATER — THEIR RELATION TO EACH OTHER AND TO THE LIQUID.

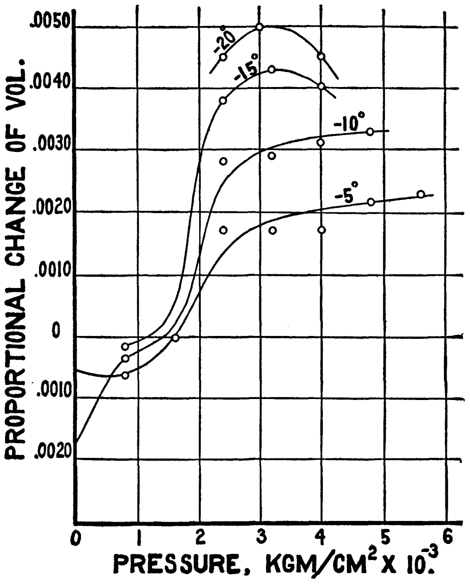

FIGURE 4. This shows as a function of the pressure the change of volume of water on passing at constant pressure from 0° to the temperature indicated on the curves.

In order to present these data systematically and clearly, reference is made at once to the final equilibrium diagram for water and the solids given at the end of this paper. (Plate 1.) It may produce less confusion in referring to this diagram to state briefly the identical relations which must be satisfied in every such diagram. There are three of these relations. At every triple point the relative positions of the three equilibrium curves must be such that if any one is produced into the region of instability, it shall fall within the angle made by the other two. If one phase is carried into another by passing across an equilibrium line at constant pressure from a low to a high temperature, then the reaction runs with absorption of heat. And, if one phase is carried into another by passing across an equilibrium line at constant temperature from a low to a high pressure, the reaction runs with decrease of volume.

The different branches of the curves will be taken up in order, beginning with I-L,[3] I-III, etc. The data to be given are the freezing pressure at any given temperature and the change of volume. From the relation between temperature and pressure on the freezing curve at different points, the slope may be found, and this, combined with the change of volume, gives the latent heat by Clapeyron's equation. The data are presented in this order: observed change of volume, calculated slope, latent heat, and then other quantities of thermodynamic interest, such as the work done in passing from one form to the other, and the change of internal energy.

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[3] Throughout, the abbreviation L will be used in referring to the liquid.

In the early part of this work up to 3500 kgm. constant reference will be made to Tammann,[4] since his are practically the only previous experiments on ice under pressure. It will be well, therefore, to briefly outline his work and show where it needs verification or completion. Tammann's work consisted essentially in following out the equilibrium curves without systematic measurements of the changes of volume. He discovered the existence of two new forms of ice (II and III), and studied their relations to water and ordinary ice (ice I). He obtained points on the equilibrium curves I–L, III–L, I–III, and I–II. The change of volume I–III and I–II was measured at a few points without any very great accuracy. The greatest possibility of question as to the results is in regard to the equilibrium curves I–III and I–II. Tammann found that these curves cross at —37° and 2200 kgm. Now it is necessary thermodynamically that a third equilibrium curve should start from the point of intersection of two equilibrium curves with a common phase. In this case the predicted equilibrium curve would be II–III. Tammann found no such curve and even maintained that no such curve was necessary, claiming that the thermodynamic argument was valid only when the two phases were present simultaneously, and that he had never been able experimentally to produce II and III together. The argument seems inadequate, however, and in this work the missing curve had been actually found. The other points of difference between this work and Tammann's are more or less minor in character; there seems to be an error in Tammann's pressure measurements of 100 kgm. at 2000, and he found a curious point of inflection in the I–L curve, which does not seem actually to exist.

For convenience, the method used will be briefly outlined. It was essentially the same as that of Tammann, and consists in plotting the displacement of the piston by which pressure is produced against pressure. Change from one form to the other is accompanied by change of volume at constant pressure. This change of phase is shown, therefore, by a discontinuity in the curve piston-displacement vs. pressure. The pressure at the point of discontinuity gives the equilibrium pressure and the volume swept out by the piston, which is determined by the amount of the discontinuity, gives the change of volume on passing from one phase to the other. The water on which these experiments were made was placed in a steel shell, open at the top, and completely surrounded by kerosene or gasolene by which pressure was transmitted. Pressure was measured by observing the change of resistance of a calibrated manganin wire immersed directly in the same chamber with the water. That the fluid transmitting pressure suffers no change of phase which is accompanied by change of volume within the limits of measurements was shown by direct experiment. Furthermore, that there is no reaction under pressure between the water and the oil, which are directly in contact, was shown by the sharpness of the freezing. See Figure 31, page 515. The effect of an impurity is to make the discontinuity less abrupt. In order to give additional evidence on this point, in the course of the experiments the water was placed in shells of steel or copper, directly in contact with kerosene or gasolene, in glass bulbs directly in contact with kerosene, and in a glass bulb with a mercury seal, the water coming in contact only with mercury and glass. The results in all cases were identical.

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[4] Tammann, Kristallisieren und Schmelzen, pp. 315–344 (Barth, Leipzig, 1903).

Three different forms of apparatus were used according to the temperature range. The first, for the middle range from –25° to +20°, was the same as that used in the work on mercury. It consisted essentially of two parts: an upper cylinder in which pressure was produced by an advancing plunger, communicating through a heavy tube with a lower cylinder containing the water under experiment and the pressure measuring coil. The lower cylinder was placed in a thermostat. The various sources of error and the corrections have been discussed in the paper on mercury. One correction had to be determined anew, since the values used in the mercury paper were not for a corresponding range of temperature and pressure. This is the correction for the thermal dilatation of the kerosene or gasolene which passes from the lower cylinder at the temperature of the experiment to the upper cylinder at the temperature of the room. The manner of determining this correction was the same as before. One correction applied to the results for mercury was avoided here, namely the correction for the variation in the room temperature. This was made unnecessary by a water jacket at constant temperature placed around the upper cylinder.

The second piece of apparatus, for temperatures from –20° to –80°, was essentially the same as the first, consisting of two parts. But the pressures for this temperature range are comparatively low, not reaching over 4000 kgm., so that it was possible to make the lower cylinder so small (1 inch o. d. by 8 inches long), that it could be placed in a thermos bottle. The connecting tube was also made much smaller so as to avoid conduction of heat into the thermos bottle. The method used in determining the change of volume had to be modified with this apparatus, since the reaction was so slow at the low temperatures. It will be described in detail later.

The third piece of apparatus for higher pressures and temperatures, 0° to 76° and 6000 to 20,500 kgm., consisted of only a single cylinder containing the water, the measuring coil, and the advancing piston. For these high pressures it was necessary to use only one piece of apparatus because of the impossibility of getting tubing to stand these high pressures over any extended time. The water was placed in a steel shell surrounded by kerosene as before. The cylinder, together with the lower part of the hydraulic press by which the piston was advanced, was placed in a thermostat. In this third form, therefore, the correction for the change of volume of the transmitting fluid on passing from one temperature to another is avoided. But at the higher pressures another correction is introduced because of the slow yield of the steel. This will be described in its place.

The data given for the ten equilibrium curves were all obtained independently of each other, at different times, with different fillings of the apparatus, and in a number of cases with different pieces of apparatus, either new pieces to replace those destroyed by explosions or pieces of a different type. The consistency of the data obtained under these various conditions is shown by the very close approximation with which the identical relations are satisfied by the independent data of the three curves at each of the three triple points.

At each triple point there are three independent checks. In the first place, the absolute values of the equilibrium pressures and temperatures are checked by the necessity for the three curves running together to a point. In the second place, the values of the change of volume are checked by the obvious condition that at the triple point I–II–III, for example, the change of volume I–II plus the change II–III must be equal to the change I–III. The third check is given by the condition for the latent heats analogous to that for the changes of volume. This third check involves, besides the values already given, the values of the slope of the three curves meeting at the triple point. This third check is the most difficult to meet and the most sensitive, as it is well known that the derivative of an experimental curve is subject to much greater error than the curve itself.

Such a triple check is afforded for the data of every one of the ten equilibrium curves at at least one point: Five of the curves are rendered still more secure by being tied down at both ends by a triple point, and the other end of a sixth curve, I–L, is checked by the already known data for 0°.

In the curves given for ΔV and the latent heat, the identical relations at the triple point were kept in view. In some cases the curve given does not seem to be the best possible through the individual points. The departure from the best curve was occasioned by the necessity of satisfying the identical relations at the triple point, and the amount of departure gives a pretty good criterion of the self-consistency of the data for the different curves.

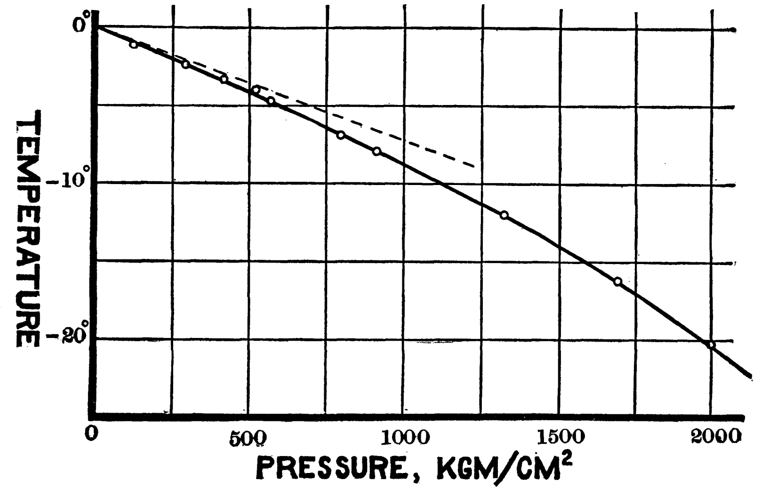

Figure 5. The freezing curve of ice I. The dotted line shows the slope at 0° computed by Clapeyron's equation.

The Curve I–L.

The points on this curve were obtained with the same apparatus as that used for mercury. No special discussion is necessary. The data were obtained on three separate occasions: February 2, February 23–24, and March 15, 1911. The equilibrium points are shown in Figure 5 and ΔV in Figure 6; the actual data are given in Table VIII. The first set is not accurate. It was taken only for fun one evening after the supply of $CaCl_2$ for running the thermostat had given out, so that the temperatures are not sufficiently accurate. These points are not shown in the diagram.

The second and third sets of readings give the equilibrium points determined with sufficient accuracy. The second set suffices to give the general shape of the entire curve, while the third set was taken with more pains at the lower pressures in order to test more definitely the existence of a point of inflection at —4° as found by Tammann. This third set was made with the apparatus directly connected to a Cailletet pump of the Société Genevoise, with a capacity of 1000 kg./cm.^{2}. As a check, the equilibrium pressures as given by the Bourdon gauge of this pump are tabulated as well as the pressures given by the manganin resistance. The slide wire of the Cary Foster bridge was especially changed for this experiment, so as to give greater sensitiveness in the measurements of resistance. The readings of the manganin gauge are to be accepted as more trustworthy than those of the Bourdon. Within the limits of accuracy of the readings, there seems to be no point of inflection on the equilibrium curve as found by Tammann, but the curvature is perfectly regular, increasing more and more rapidly at the lower temperatures and higher pressures. The point of inflection found by Tammann may very possibly be due to errors in the pressure measurements. His values for the pressures in the neighborhood of 2000 are nearly 100 kgm. higher than those found here. The effect of introducing such an error into the gauge readings at some point on

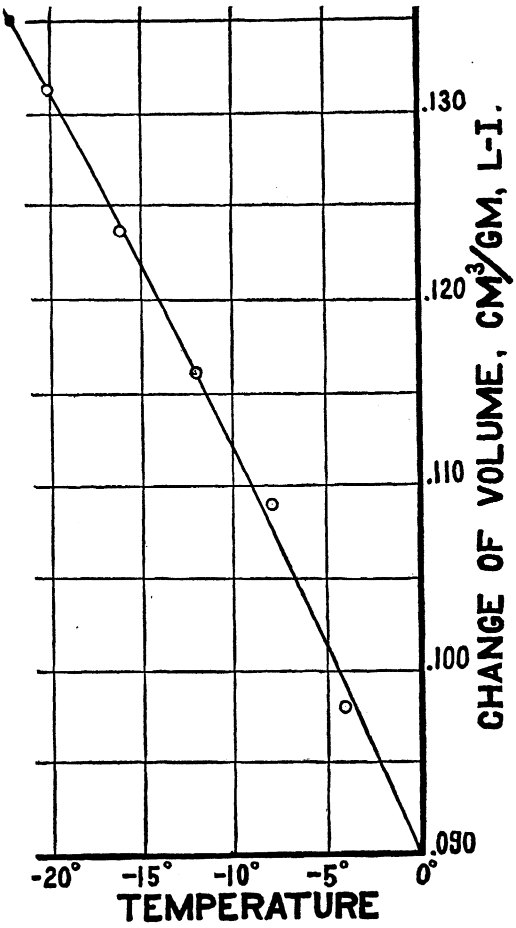

Figure 6. The change of volume when ice I melts to the liquid.

the way up would be to give exactly such a point of inflection as he found.

One check on the accuracy may be obtained from the known slope at 0°, calculated by Clapeyron's equation from the known latent heat and the change of volume. This slope is given by the equation

TABLE VIII.

Data for the Equilibrium Curve Ice I-Water.

Date, 1911.	Temp. C.°.	Pressure, kgm./cm.^{2}.		Δv, cm.^{3} per gm.		
		From Resistance Measurement.	Bourdon Gauge.	Uncorrected.	Corrected for Dilatation of Gasolene.	Corrected for Distortion of Cylinder. (Final value.)
Feb. 2	−20.6	2100				
	−18.7	1890				
	−14.80	1580				
	−12.40	1370				
23	−20.15	2000		0.1337	0.1312	0.1316
	−16.15	1690		1257	1236	1238
24	−12.00	1320		1178	1160	1162
	− 7.9	910		1103	1090	1091
	− 4.0	520		0991	0980	0980
March 15	− 6.9	788	798			
	− 4.75	565	568			
	− 3.3	416	418			
	− 2.3	281	288			
	− 1.1	122	121			

$$\frac{d\tau}{dp} = \frac{\Delta v \cdot \tau}{\Delta H}.$$

Using the following values : $\Delta V = 0.0900$, $\tau = 273.1$, $\Delta H = 79.82$ gm. cal., 1 gm. cal. $= 42.66$ kgm. cm., we find

$$\frac{d\tau}{dp} = -0.00722.$$

It is to be noticed that this value is lower than the calculated value usually given. This is because of the low value used for ΔV, which is taken from the most recent work of Leduc.[5] The effect of this change is to bring the calculated value into better agreement with experimental values. Thus Dewar[6] found recently for $\frac{d\tau}{dp}$, 0.0072. The slope at the origin as just calculated is shown by a dotted line in the diagram. The agreement is within the limits of error.

Even over this very low pressure range there are practically no other results to compare these with. Tammann is the only other observer who has gone to high enough pressures to find the direction of curvature of the curve, which agrees with that found here. Dewar has published results up to 250 kgm., and stated without publishing the data that the curve remains linear up to 700 kgm. The departure from linearity found above is about 6 per cent at 700. Several other accounts have been published of the effect of pressure on the freezing of ice, but the work has either been done only to a few atmospheres, or else the work to high pressures has been only qualitative, like that of Mousson.[7]

The second set of readings above gives the only determination of the change of volume made in the present work. The procedure in determining four of these five points was the same as that used for nearly all the other determinations with water as well as with mercury. This consists in plotting piston displacement against pressure during decreasing pressure. This has the advantage at higher pressures of almost entirely eliminating the effect of elastic after-effects in the containing vessel, but this procedure is less essential at lower pressures. For all ordinary substances this procedure means that the change of volume is measured during melting and has the advantage that it gives perfectly sharp values, it being impossible to overrun the melting curve. But here, due to the fact that ordinary ice is less dense than the liquid, the method gives the change of volume during freezing instead of melting, so that it is possible to considerably overshoot the mark before solidification sets in. The change of volume is so large during freezing, however, that this is no practical disadvantage, as it is with substances showing a smaller change of volume. The fifth point of the above series was obtained in the inverse way, during melting, proceeding from low to high pressures. The pressure corresponding to —4° is so low that the elastic after-effect must be small, but still it is noteworthy that this point shows the greatest deviation from the straight line. This inverse procedure at —4° was necessary in this case because of the low pressures, the friction of the packing being so great that pressure could not be reduced sufficiently below the equilibrium pressure to induce solidification from the subcooled liquid when the regular procedure of running from high to low pressures was adopted.

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[5] Leduc, C. R., **142**, 149–151 (1906).

[6] Dewar, Proc. Roy. Soc. Lon., **30**, 533–538 (1880).

[7] Mousson, Pogg. Ann., **105**, 161–174 (1858).

The correction applied to the change of volume for the thermal dilatation of the gasolene (the fluid transmitting pressure in this set of experiments), was not determined directly at all points of the curve, but only at the two end points. At 0° the correction is 0.9 per cent, and at —22° is 2 per cent. The correction was assumed linear for intermediate points. It makes no difference within the limits of error whether temperature or pressure is taken as the independent variable of this linear relation, and there seems little probability that the error so introduced can exceed this 0.1 per cent. The tables give the values corrected both for the thermal dilatation of the gasolene and for the elastic deformation of the cylinder. This latter correction is 0.2 per cent at the maximum.

The values of ΔV are shown in Figure 6. The open circles are the observed points. The solid circle at —22° was not an observed point, but is the value required at the triple point by the conditions of consistency with the other data. In the ΔV diagrams for the other equilibrium curves the values at the triple points are indicated in the same way.

As an additional check on the values found here there is the known change of volume at 0° as found by other observers. The recent work of Leduc seems the most accurate. He gives for the value of the density of ice at 0°, 0.9176, from which the change of volume is found to be 0.0900 cm.^{3} per gm. The value of ΔV at 0° as found by Leduc is taken as the origin in the diagram. It is seen that the other points are perfectly consistent with this value, thus confirming the accuracy of the method. The relation connecting change of volume with temperature is nearly linear, the curve being slightly concave toward the temperature axis. Four of the points, including Leduc's, lie sensibly on the curve; one is 1 per cent too high, and the other 1.5 per cent too low.

This value of Leduc is higher than that of most other observers, but the discrepancy seems to be due to occluded air, which Leduc took particular pains to exclude. In these experiments in which the water was frozen under pressure, any dissolved air, naturally, can have only very little effect. Leduc's value, therefore, seems best for this comparison.

It will be well here to explain the sign convention used uniformly throughout the paper. A change of volume is taken as positive if the volume increases when the reaction runs in the indicated direction. Thus ΔV L–I is positive (water expands when it freezes to ordinary ice) but ΔV I–L is negative. Similarly the latent heat, ΔH, is positive when heat is absorbed during the reaction, and ΔE, the change of internal energy, is positive when the internal energy increases. ΔH for the reaction L–I is negative, but positive for I–L. In general, as already explained, ΔV is positive when the reaction runs from high to low pressure and ΔH is positive when the reaction runs from low to high temperatures.

TABLE IX.

Latent Heat, etc., on Equilibrium Curve Ice I–Water.

Temp. C.°.	Pressure, kgm./cm.².	Δv. cm.³/gm.	$\frac{dp}{dt}$.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. (Latent Heat) $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. (Change of internal Energy) $\frac{\text{gm. cal.}}{\text{gm.}}$.
			Directly from Curves.	Adjusted.			
−20	1970	−.1313	74.6	74.0	6.06	57.7	63.6
−15	1590	−.1218	86.0	84.8	4.52	62.5	67.0
−10	1130	−.1122	99.0	98.4	2.96	68.0	71.0
− 5	610	−.1016	116.0	115.5	1.45	73.7	75.1
0	0	−.0900	138.5	138.5	0.00	79.8	79.8

From the curves giving the equilibrium points and the changes of volume, the various data needed for computing the latent heat and the change of internal energy may be obtained. These are given in Table IX. for even temperature intervals. The values of ΔV were taken from the line drawn through the observed points. Two values of $\frac{dp}{dt}$ are tabulated. The first set of values was obtained by graphical construction from the equilibrium curve at different points, these values of $\frac{dp}{dt}$ plotted and a smooth curve drawn through them. The first tabulated values of $\frac{dp}{dt}$ are obtained from this smooth curve. With these values of $\frac{dp}{dt}$, ΔH was calculated. It was then necessary to adjust the values of ΔH slightly so as to satisfy the identical relations at the triple point. These new values of ΔH are tabulated. The change in the value of ΔH demands a corresponding change in the values of $\frac{dp}{dt}$ which are given in the second column. These latter values are to be taken as the most probable values. The difference between the two columns shows the amount of adjustment necessary, and gives an idea of the accuracy of the data. Of course, as already explained, the slope is very much more sensitive to slight errors than the observed values of p and t themselves. This same process of adjustment has been used on all the equilibrium curves. In some cases, where $\frac{dp}{d\tau}$ is very small, no change has been necessary. The data of Table IX. are shown graphically in Figure 7.

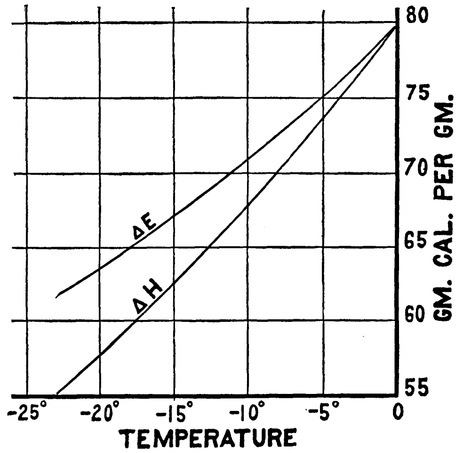

FIGURE 7. The latent heat and the change of internal energy on the I–L curve.

The data give some hold on the actual compressibility of the solid at different points on the equilibrium curve. At 0° this may be calculated without approximation from the observed data. The thermal dilatation and compressibility of water at 0°, and the thermal dilatation of ice at 0°, are already known. These present data give the change of ΔV with temperature and pressure on the equilibrium curve. These four quantities evidently suffice to determine the compressibility of the solid at 0°, for we have for small changes of p and t,

$$V_1(p,t) = V_1(0,0) + \left(\frac{\partial v_1}{\partial p}\right)_t dp + \left(\frac{\partial v_1}{\partial t}\right)_p dt,$$

$$V_2(p,t) = V_2(0,0) + \left(\frac{\partial v_2}{\partial p}\right)_t dp + \left(\frac{\partial v_2}{dt}\right)_p dt,$$

where the subscript (1) denotes the liquid and (2) the solid.

$$\Delta V(p,t) = V_2(p,t) - V_1(p,t) = \Delta V(0,0) + dp\left[\left(\frac{\partial v_2}{\partial p}\right)_t - \left(\frac{\partial v}{\partial p}\right)_\tau\right] + d\tau\left[\left(\frac{\partial v_2}{\partial t}\right)_p - \left(\frac{\partial v_1}{\partial \tau}\right)_p\right].$$

This holds for any values of *dp* and *dt*. On the equilibrium curve,

$$d\tau = \frac{d\tau}{dp}\,dp,$$

and we have

$$\frac{d\Delta V}{dp} = \frac{d\Delta V}{d\tau}\cdot\frac{d\tau}{dp} = -\left(\frac{\partial v_2}{\partial p}\right)_\tau + \left(\frac{\partial v_1}{\partial p}\right) + \frac{d\tau}{dp}\left[-\left(\frac{\partial v_2}{\partial \tau}\right)_p + \left(\frac{\partial v_1}{\partial \tau}\right)_p\right].$$

Everything in this equation is known except $\left(\frac{\partial v_2}{\partial p}\right)_\tau$.

We have $\left(\frac{\partial v_1}{\partial p}\right)_\tau = 0.0_452$ kgm./cm.^{2} (Amagat),

$$\left(\frac{\partial v_1}{\partial \tau}\right)_p = -\,0.0_457,$$

$$\left(\frac{\partial v_2}{\partial \tau}\right)_p = +\,0.0_3152 \text{ (Vincent),}^{8}$$

$$\frac{d\tau}{dp} = -\,0.00722 \text{ [already computed; see p. 468].}$$

$$\frac{d\Delta V}{dt} = -\,0.00200 \text{ [from these experiments].}$$

Substituting these values in the above expression, we find

$$\left(\frac{\partial v_2}{\partial p}\right)_\tau = -\,0.0_436.$$

The compressibility of ice, with the larger volume, is therefore about 1/3 less than the compressibility of the liquid. There seem to be no published experimental data with which to compare this value.

The Curve I–III.

The existence of this new variety of ice, III, was discovered by Tammann, who obtained it by increasing the pressure on ordinary ice to about 2500 kgm. at temperatures between —22° and —60°. The nota-

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[8] Vincent, Phil. Trans. A, **198**, 463–481 (1902).

tion used here is the same as that used by Tammann. In the present work this variety of ice was found in another way, coming from high to low pressures at about —22°, and from the domain of stability of a variety of ice stable only at higher pressures. It was obtained first with the same apparatus as that used on the I–L curve. Two points on equilibrium curve I–III and two unsatisfactory measurements of the change of volume were made with this apparatus, but all the subsequent determinations were made with the apparatus especially designed for low temperatures. A short description of this new apparatus will not be out of place.

This had three different pressure chambers instead of only two as formerly. The upper cylinder in which pressure was produced by the advance of the piston was the same as that used before. This was jacketed with running water from a large tank, so as to be maintained at a constant temperature. Communicating directly with this, and exposed freely to the air of the room, was a block of nickel steel with provisions for three connections. In one of these holes for connections was placed the manganin resistance plug with which pressure was measured. No temperature correction had to be applied to the readings of this, therefore. The third connection in the block was to the cylinder containing the water to be experimented on. This cylinder was of hardened nickel steel, 8 inches long, 1 inch o. d., and 1/2 inch i. d. The water to be experimented on was placed directly in the cylinder, nearly filling it. The remainder of the cylinder was filled with gasolene communicating through the connecting block with the pressure-producing cylinder. Some hesitation was felt at first about allowing the water to completely fill the interior of the cylinder, instead of being placed in a cylinder exposed to pressure on all sides. Fear was felt that the water in freezing might so expand itself against the sides of the cylinder as to be able to support an appreciable stress, so that a hydrostatic pressure applied by means of the gasolene to the upper part of the frozen ice cylinder would not be transmitted uniformly to all parts of the mass of ice. In the first few experiments an attempt was made to avoid the possibility of the effect by providing means for the gasolene to penetrate to the neighborhood of all parts of the ice. This was done with a tube of very thin sheet copper, closed at the bottom, but open at the top to the gasolene, placed axially in the cylinder, and extending throughout the mass of water. The precaution proved needless, however, since there were no discrepancies to be ascribed to this cause when the device was omitted.

It was necessary to use gasolene as the transmitting fluid because of the low temperatures. Kerosene becomes too stiff to transmit pressure, and the gasolene itself gave evidence of considerable viscosity at the lower temperatures. Attempt was made to use a still lighter oil to avoid altogether this viscosity. Pentane was tried, but after a number of failures had to be abandoned. There is evidently some action under pressure between the pentane and either the water or the ice. The action seems to be one of solution. In every case water found its way sooner or later through the long connecting tube to the manganin resistance coil, where it short-circuited the coil, making measurements impossible.

The nickel steel cylinder containing the water was supported from above by means of the connecting pipe in a cylindrical Dewar flask, 2 inches diameter and 10 inches long. The low temperature was obtained with solid CO_2 and ether, or usually CO_2 and gasolene, this being much cheaper and giving nearly as low a temperature as the ether. No thermostatic regulation was used with the apparatus. The thermal insulation provided by the bath proved sufficient so that the slight amount of regulation necessary could be performed from time to time by hand, by dropping in small masses of solid CO_2. The bath liquid was stirred by blowing bubbles of air into it through a tube reaching to the bottom of the flask. It was possible with very little effort to keep the temperature constant to 1/2°, which was sufficient for most requirements, since in the region of these experiments the equilibrium pressure is affected only slightly by changes in temperature. Greater constancy of temperature was attained by the exercise of a little more care when this was necessary.

Temperature was measured with a nickel resistance thermometer. This was a coil of bare nickel wire wound in spiral grooves on a hard rubber cylinder, which was immersed in kerosene in a thin, tightly fitting tube of glass. The top of this tube was carefully stoppered to prevent the condensation of moisture around the leads. The glass tube, 3/8 inch o. d., was immersed directly in the temperature bath. The response to changes of temperature was always very prompt. The resistance of this wire was measured on the same bridge wire of the same Carey Foster bridge as that on which the measurements of the resistance of the manganin coil for pressure were made. Either the nickel or the manganin resistance, with the appropriate extension coils, could be connected with the bridge wire by two double-throw mercury switches in paraffin blocks. The temperature was ordinarily read both before and after the readings of pressure and piston displacement. The coil was calibrated by comparison at 0°, –50°, and –80° with a nickel resistance thermometer of Leeds and Northrup, which had been calibrated at the Bureau of Standards. The sensitiveness was sufficient to detect changes of 0°.03. The coil was tested for permanent changes, elastic after-effects, etc., by frequent calibrations in melting ice at 0°. That it was perfectly satisfactory is shown by the fact that the zero has not changed by 0°.03 since the coil was set up.

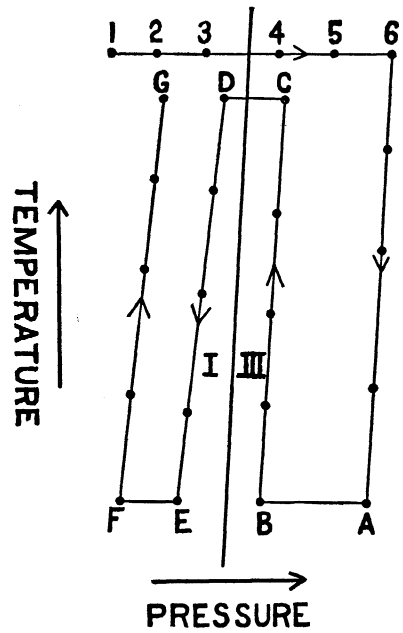

FIGURE 8. Shows the cycles described in finding the change of volume I–III.

A special method for determining the change of volume at the low temperatures was made necessary by the extreme slowness of the reaction. At the higher temperatures, between —20° and —30°, the reaction runs rapidly enough so that the ordinary procedure is available, but at lower temperatures this is not possible. On one occasion, such an attempt was made at —70°. After four hours waiting at a pressure several hundred kgm. removed from the equilibrium pressure, the reaction had not yet shown any signs of drawing to completion, and the attempt was given up. The new method is made possible by the fact that the equilibrium pressure is very nearly constant. Figure 8 illustrates the method. The first part of the process consists in getting the change of volume by the ordinary method at some temperature where the reaction runs with convenient rapidity. This consists in measuring the piston displacement at constant temperature at several points on each side of the equilibrium line indicated at (1), (2), (3), (4), (5), (6). After reaching (6) the piston displacement is kept constant, but the temperature is reduced, the water now being in the form of ice III. The pressure is measured at several points with decreasing temperature until the point A is reached. The apparatus is so small that complete temperature equilibrium is attained in at most 5 minutes after changing the bath temperature. At the point A the pressure is reduced at constant temperature by changing the displacement, until the point B is reached, still to the right of the equilibrium line. From B, temperature is raised at constant displacement to the point C. Here the pressure is lowered to D, the reaction now running with sufficient speed because of the higher temperature. From D, two excursions to low and then back to high temperatures are made exactly as from (6), the water now being in the form of ice I. The result of all these manœuvres is that we have sufficient data to find the displacement corresponding to any temperature and pressure, and so the displacement on opposite sides of the equilibrium line corresponding to the two phases I and III. The difference of this displacement at any temperature is evidently the same as if the reaction had run at that temperature, but the slowness of the reaction is avoided. The change of volume is calculated directly from the difference of displacements as usual. It was in general necessary to measure the displacement at at least three points on each side of the equilibrium line, since the relation between displacement and pressure is not sufficiently linear to allow a linear extrapolation from two points to the equilibrium line. For greater security, four or five points were usually taken.

The data are such that they contain internal evidence of their self-consistency. After a complete cycle like the above, the starting point ought to be reached again, if there has been no change in the apparatus in the meantime. This condition was always approximately fulfilled, the piston returning within a few thousandths of an inch to the original position. Failure to return exactly to the starting point is probably due partly to elastic after-effects in the steel cylinders, and partly to wearing away of the rubber packing on the end of the piston. There was never any leak. The slight discrepancy was corrected for by assuming that it had grown uniformly with the time. It will be noticed that the cycle as described above is such that the effect of any such error is at a minimum, since the two paths nearest the equilibrium curve on either side were described in succession.

The method is applicable here because of the fact that the equilibrium lines run so nearly parallel to the lines of constant displacement that it is possible to approach very near to the equilibrium line over the entire range. The method evidently would not apply without modification to points on the I–L curve, for example.

The slowness of the reaction which made necessary a modified method of determining the change of volume is also evidently going to have its effect on the equilibrium determinations. At the low temperatures, the reaction runs so slowly that it requires a very long time for pressure to return to the equilibrium values, if it has once been changed. The behavior was such as to give the impression that the equilibrium pressure might never be reached, there being a domain of indifference within which the viscosity is sufficient to keep the reaction from running, even if the equilibrium conditions are not satisfied. This has been stated to be the fact by Tammann. The equilibrium points at the low temperatures were found by approaching as close as practicable to equilibrium from each side, and taking the mean. The tables of the actual data show how broad the band of indifference is and how rapidly it increases in breadth at the low temperatures.

For these determinations with this new piece of apparatus, ice III was usually obtained from ice I. The procedure was to freeze water to ice I at a low pressure, and then increase the pressure on ice I at a temperature in the neighborhood of —30°. It was always necessary to pass considerably beyond the transition curve before the reaction started. On several occasions at —28° the pressure was carried so far over the I–III curve as to arrive at the prolongation of the I–L curve, at which melting took place immediately, it never being possible to carry a solid into the domain of the liquid. I melts to the liquid even if the liquid is relatively unstable with respect to another solid phase. At the temperature —28° it was never possible to keep the unstable liquid long enough to make an accurate determination of the equilibrium pressure. The rough values fell within the limits of uncertainty on the smooth prolongation of the I–L curve. When the phase III did appear at temperatures above —30°, the reaction from I to III ran with explosive rapidity. Sometimes it was possible to hear a sharp click in the apparatus announcing the sudden change of volume.

Aside from the fact that it is possible to pass over the boundary line between two solid phases without the reaction running, the actual amount of possible trespassing has little significance. It is changed by alterations in the size and shape of the containing vessels, is affected by slight impurities, and most of all depends on the element of time. It may be mentioned, however, that under pressure the viscosity of the substances seems to be so great that mechanical shock has little if any part in starting the reaction, as it does under ordinary circumstances. It was never found possible to start a reaction from an unstable phase by smart blows on the outside of the apparatus with a hammer. This was tried both when the unstable phase was a solid and a liquid.

After the phase III had once been obtained, the other points on the equilibrium curve were obtained with decreasing temperature. At every new temperature, the piston was pushed in a little, the pressure then falling back to the equilibrium value, and then the piston was withdrawn slightly, pressure rising to the equilibrium value. The mean of these was taken as the equilibrium pressure. Sometimes at the higher temperatures, where the reaction velocity is high, equilib-

TABLE X.

Data for the Equilibrium Curve Ice I–Ice III.

Date, 1911.	Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv. cm.^{3}/gm. Corrected Value.	Date, 1911.	Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv. cm.^{3}/gm. Corrected Value.
Feb. 16	−22.80	2120	−0.1910	April 6	−52.5	2100^{-}	
	−25.25	2120	−0.1861		−50.0	2110^{+}	
Mar. 24	−32.0	2150^{-}			−62.0	2000^{-}	
	−31.7	2150^{+}			−61.2	2100^{+}	
	−24.7	$2110^{\pm}$			−32.8	2150^{-}	
Mar. 29	−33.8	2170^{-}			−32.6	2150^{+}	
	−28.7	2150^{+}			−26.5	$2120^{\pm}$	
	−26.7	2140^{V}		April 18	−27.6	2110^{+}	
	−23.5	2130^{V}			−22.4		−.1831
April 5	−33.4	2170^{+}			−29.1		.1903
	−33.0	2160^{-}			−35.7		.1966
	−28.1	$2150^{\pm}$			−41.7		.1948
	−23.1	$2140^{\pm}$			−49.6		.2018
	−21.5	$2140^{\pm}$			−56.6		.2042
April 6	−26.4	2120^{+}			−63.8		.2059
	−25.9	2100^{-}			−70.8		.2071
	−31.0	2110^{+}		April 20	−23.3	$2134^{\pm}$	
	−30.7	2110^{-}			−24.5	$2136^{\pm}$	
	−38.6	2120^{-}			−27.8	$2153^{\pm}$	
	−38.4	2130^{+}			−31.5	$2163^{\pm}$	
	−43.5	2130^{-}			−37.2	$2182^{\pm}$	
	−42.5	2150^{+}			−46.0	$2179^{\pm}$	

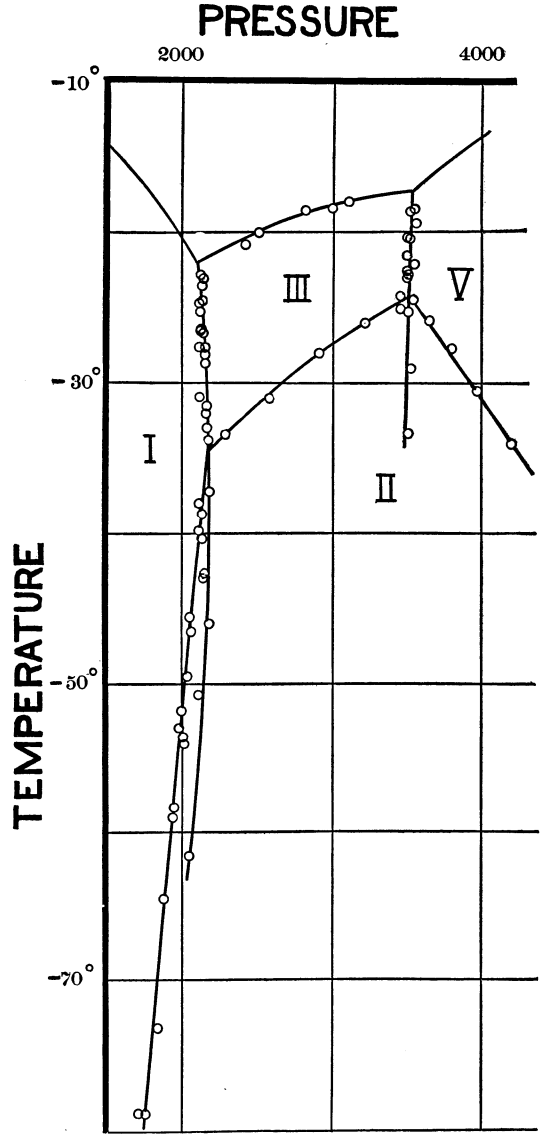

Figure 9. The various equilibrium curves between I, II, III, V, and the liquid.

rium was approached from only one side. By proceeding in this way from high to low temperatures, it was possible to prolong the curve considerably into the region of stability of II. A point was thus found at —62°.0, showing a subcooling of 28°. If the pressure had been increased on ice I at this temperature, ice II and not ice III would have separated out.

The actual data are given in Table X. Those of February 16 were obtained with the same apparatus as that used for the mercury; all the others with the smaller apparatus for lower temperatures. The plus or minus signs after the pressures show whether the value was approached from above or below. Three different manganin coils were used in making the measurements. The data of April 6 were obtained with a new coil which had not yet been sufficiently seasoned. For this reason the data of April 6 are slightly in error as to the absolute value of the pressure, but are competent to show the shape of the equilibrium curve. The data of April 20, taken with especial care to show the actual shape of the equilibrium curve, give more significant figures than one is entitled to for the absolute pressure, but the variation of pressure is accurately indicated by the figures given.

The equilibrium points are shown in Figure 9, in which are shown also the other equilibrium curves in the vicinity. The shape of the curve is given by the points of April 6 and 20, which agree, but the best value for the absolute pressure is to be given by the mean of the points at the upper end of the curve. On the same pressure and temperature scale as the complete diagram for ice and water this equilibrium curve appears nearly vertical, but on the scale shown here it is seen to have unmistakable curvature, being concave toward the temperature axis, and at one part parallel to that axis. At this point of parallelism, the latent heat of transformation is zero; above it is positive, below negative. This point is approximately at —40° and 2150 kgm.

The equilibrium curve I–III as found by Tammann shows the same general shape, concavity toward the temperature axis. But Tammann's vertical tangent is between —40° and —50°. The total change of pressure from the triple point at —22° to the maximum is practically the same, 50 kgm., but Tammann does not find so pronounced a curvature below the maximum as is found here. On the whole, however, the agreement in the shape of the curve as found in these two independent determinations is as good as could be expected, particularly when it is remembered that the discrepancies are at the low temperatures where the reaction runs very slowly. But the actual value of the pressure as found by Tammann at —22° is higher than that found here, 2200 against 2115. Tammann's pressure measurements were made with a Bourdon gauge, which is not accurate at high pressures. There are two pieces of evidence to show that Tammann's pressures may be wrong; the supposed inflection point on the I–L curve, which has been already mentioned, and the behavior of the I–III curve above the I–II–III triple point, which will be dealt with later.

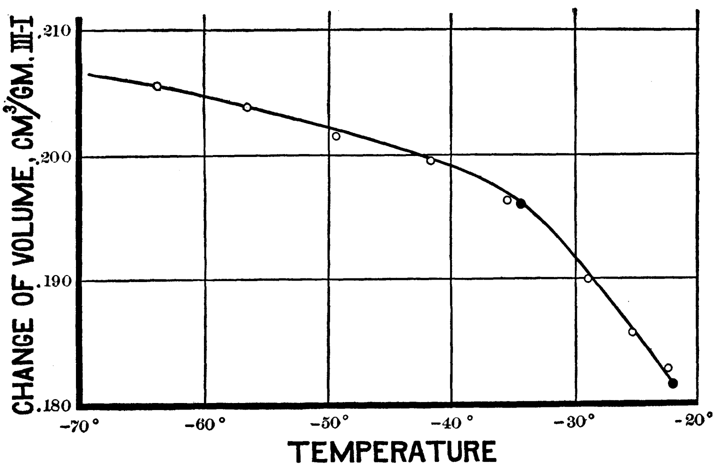

Figure 10. The change of volume III–I.

The values for the change of volume obtained on April 18 with the method described are given also in Table X., and shown in Figure 10. The most striking feature is the enormous value of the change, being about 20 per cent. The values extend into the unstable region over a temperature interval twice the interval of stability, which is from —22° to —35°. The values given have been corrected in the usual way for the elastic distortion of the cylinder and the thermal dilatation of the gasolene. Owing to the wide temperature range, this latter correction is unusually large, rising to 6 per cent at the lowest temperatures. The curve drawn through the points is forced a little so as to give consistent results at the triple points, at —22° passing about 1/4 per cent too low and at —35° 1/4 per cent too high.

The actual procedure in getting these change of volume points was not exactly the ideal one described above. Below —35°, III is unstable, and the reaction to II might run at any time. The path 6 A (Figure 8) was described successfully and two points found on the lower end of BC before the reaction to II ran. On raising the temperature above the II–III curve, the reaction ran back to III, so that at C the phase present was III, as it should be. The line 6 A was perfectly straight; it was assumed, therefore, that the line CB would also have been perfectly straight if it had been possible to trace it out for its entire length.

TABLE XI.

Latent Heat, etc., on Equilibrium Curve Ice I–Ice III.

Temp. C.°.	Pressure, kgm./cm.^{2}.	Δv. cm.^{3}/gm.	$\frac{dp}{dt}$.	$p\Delta V$. gm. cal./gm.	ΔH. gm. cal./gm.	ΔE. gm. cal./gm.
−60	2117	.2049	5.4	10.13	−5.5	4.6
−50	2160	.2023	2.0	10.24	−2.1	8.1
−40	2178	.1992	−0.6	10.17	+0.7	10.9
−30	2156	.1919	−3.2	9.69	3.5	13.2
−20	2103	.1773	−5.3	8.74	5.6	14.3

The upper ends of the lines of equal volume for the phase I, that is, the lines ED and FG above the triple point at −35°, bear less and less to the right, and at their extreme upper ends are actually bearing to the left. This would mean a negative thermal dilatation for ice I at these temperatures. The effect deserves to be investigated for its own sake. The effect is so slight as to make very little difference for the purposes of this paper, however, and it was not investigated further. That there may be such an effect is borne out by the rather sharp change in the curvature of the ΔV curve at the triple point −35°, while the accuracy of the ΔV curve is made very probable by the closeness with which it checks at the two triple points. Pettersson[9] claims to have found that ordinary ice at atmospheric pressure shows a negative dilatation between −35° and −25°.

Table XI. gives the values taken from the equilibrium and the change of volume curves for the various quantities involved in the determination of the latent heat and the change of energy. The values of ΔE and ΔH are shown graphically in Figure 11. The internal energy of III is greater than that of I, and practically all this change of energy comes from the mechanical work absorbed when I

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[9] Pettersson, Vega Expedition, vol. 2 (1883).

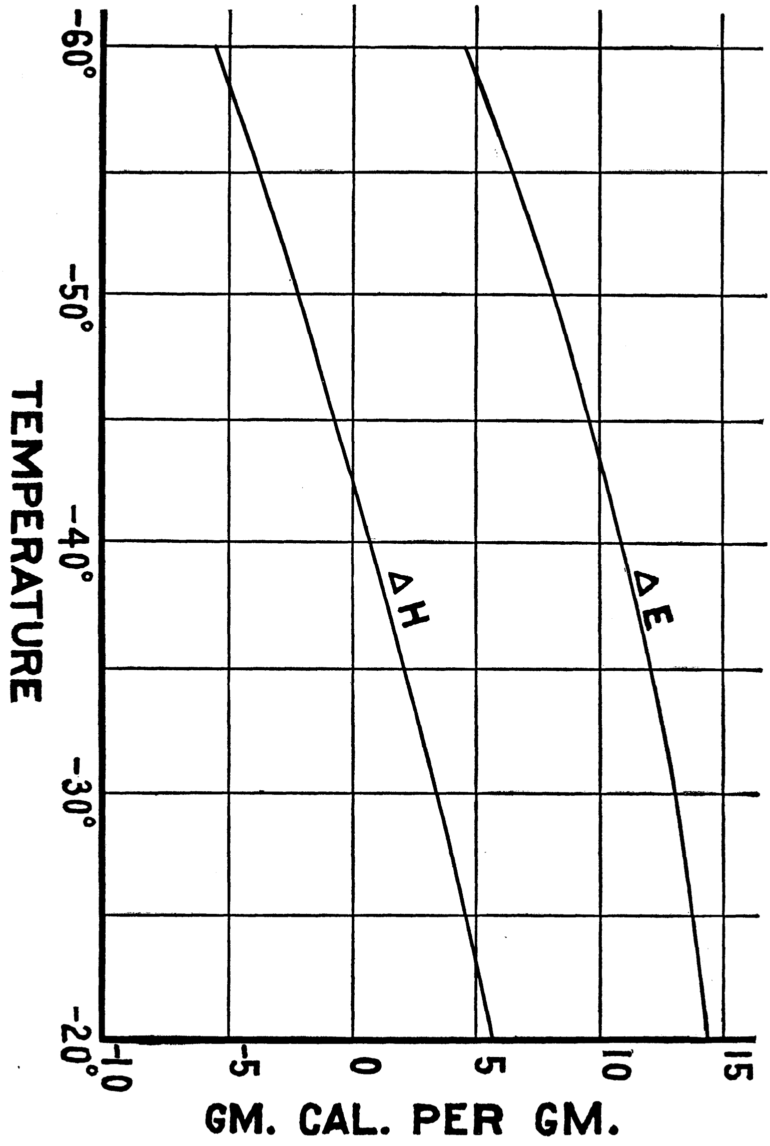

FIGURE 11. Shows the latent heat and the change of internal energy when I passes to III.

passes to III. The latent heat is small; above −40° I absorbs heat on passing to III, below −40° it gives out heat.

The Curve III–L.

The points on this curve were more difficult to obtain accurately than those on any of the other nine equilibrium curves. This is because of the extreme slowness of the reaction, accounted for in part by the comparatively small change of volume and the large heat of reaction. This does not prevent, however, a fairly accurate knowledge of the properties of the curve, since the curve is short, reaching over only 1500 kgm., and it is tied down by a triple point at either end.

The apparatus used for this curve was that of the mercury determinations, temperature being kept constant with a thermostat. This was necessary because of the great effect of temperature on the equilibrium pressure on this curve.

Five points on the equilibrium curve were obtained, and two on the change of volume curve. These are shown in Table XII. and Figures 9 and 12. The equilibrium points are satisfac-

TABLE XII.

Data for the Equilibrium Curve Ice III–Water.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.^{2}.	ΔV cm.^{3}/gm. Corrected Value.
Feb. 1	−18.55	2820	
	−20.00	2510	
	−17.95	3110	
Feb. 16	−18.40	3000	.0301
March 2	−20.80	2420	.0373

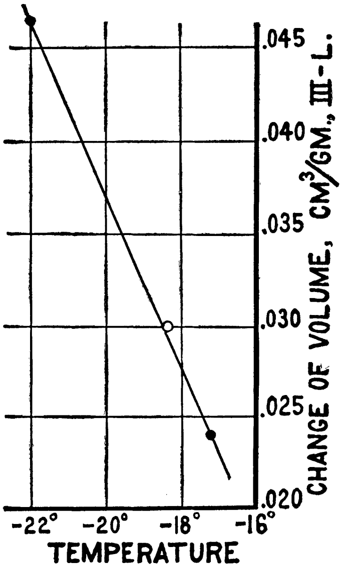

Figure 12. The change of volume when III passes to the liquid.

tory enough. The greatest difficulty was found with the ΔV points. These are evidently irregular, but with the two other known points on the curve at the triple points, the curve itself cannot be far from that

TABLE XIII.

Latent Heat, etc., on the Equilibrium Curve Ice III–Water.

Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Δv. $\frac{\text{cm.}^3}{\text{gm.}}$.	dp/dt.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal}}{\text{gm.}}$.
			Directly from Curves.	Adjusted.			
−22.0	2115	0.0466	180	186	2.31	50.9	48.6
−20.0	2510	.0371	240	246	2.18	54.1	51.9
−18.5	2910	.0301	326	320	2.05	57.4	55.4
−17.0	3530	.0231	450	443	1.90	61.4	59.5

drawn. The relation between temperature and change of volume was assumed linear within the limits of error.

Three points on this equilibrium curve were found by Tammann. The shape of his curve agrees with that found here within the limits of error, but the absolute values of the pressure found by Tammann are higher than those given, as already explained. Tammann gives no values for ΔV on this curve.

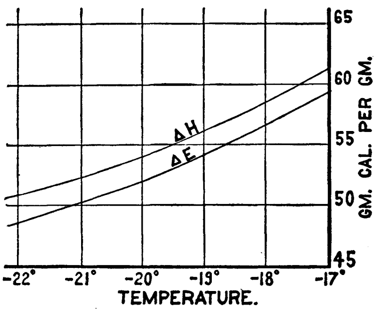

Figure 13. The latent heat and the change of internal energy when III passes to the liquid.

The values deduced from these curves for ΔH and ΔE are given in Table XIII. and in Figure 13. Very slight changes in the coordinates of points on the equilibrium curve make enormous changes in the value of the slope and ΔH. Thus, raising the upper triple point from —17°.2 to —17°.0 changed the calculated value of ΔH from 94 to 64. This latter value is taken as the more nearly correct, because it checks with the other values at the triple point, even, though the V–L curve has to be slightly raised to pass through the point.

The Curve I–II.

We return now to the curve meeting the I–III curve at the lower temperatures, the I–II curve. The points on this curve were found with the low temperature piece of apparatus.

The data, shown in Table XIV., were obtained on five separate occasions with three different manganin resistance coils. The first three sets, on March 24, 29, and April 5, were obtained before the points on the I–III curve were obtained at the low temperatures.

The whole investigation at the low temperatures was approached with the prejudice that Tammann must have been wrong. In particular, the existence of two separate modifications of ice, II and III, with only slightly different properties, was thought to be explicable by some instrumental error. This prejudice was strengthened by Tammann's failure to find the triple point I–II–III, or any points on the melting curve of II, although he must have passed over this curve if there were such a one. His failure to find the II–L curve was difficult to explain because the reaction from solid to liquid always runs, and in this case the accompanying change of volume is fairly high. The work of the first three days still further strengthened the impression of error in Tammann's work. It showed conclusively that there was a modification of ice different from III in equilibrium with I at low temperatures, but seemed to show that this was not the variety supposed by Tammann. The points of the three days all lay on the same curve, which was headed exactly for the intersection of the I–L and the V–L curves both prolonged into the region of stability of III. It seemed probable, therefore, that Tammann's II was nothing but our V in the unstable region.

The determinations of these two days were made with two different coils, one a well seasoned one that had been maltreated in many explosions, and the other a brand new one. After several days' work suspicion was drawn to these coils and they were checked by measuring with them the equilibrium pressure on other already well established curves. Both on the I–III curve and the III–V curve they gave results consistent with each other but about 100 kgm. higher than the previous values. There seems no reason to doubt, therefore, that these coils were both in error and, by a stroke of luck, by the same amount. This disposed definitely of the idea that the new ice was V subcooled. The values tabulated are corrected by this quantity 100 kgm. There seems no reason why these readings should be entirely discarded; they

TABLE XIV.

Data for the Equilibrium Curve Ice I–Ice II.

Date, 1911.	Temp. C.°.	Pressure, kgm./cm.^{2}.	Date, 1911.	Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
March 25	−64.7	1960	April 5	−63.7	1910^{+}	
	−66.8	1950		−53.6	2000^{+}	
	−65.2	1960		−52.2	1970^{-}	
	−59.2	1900^{-}	April 6	−69.5	2020^{+}	
	−58.7	1980^{+}		−76.5	1670^{-}	
	−52.1	1980^{-}		−58.7	1900^{-}	
	−51.5	2020^{+}		−58.0	2000^{+}	
	−45.7	2040^{-}		−50.0	2010^{-}	
	−45.5	2060^{+}		−49.0	2060^{+}	
	−38.0	$2110^{\pm}$		−40.1	2100^{-}	
March 29	−78.8	1690^{-}		−39.5	2120^{+}	
		1840^{+}		−53.4	2000^{-}	
	−54.1	1990^{-}		−54.5	2040^{+}	
	−53.0	2030^{+}	April 18	−36.9	$2110^{\pm}$	
	−46.7	2050		−35.7		0.2187
	−46.4	2070		−41.7		.2172
	−40.8	2130^{-}		−49.6		.2169
	−40.0	2130^{+}		−56.6		.2159
April 5	−78.8	1780^{+}		−63.8		.2154
		1640^{-}		−70.8		.2145
	−65.6	1850^{-}		−78.0		.2145

seem perfectly satisfactory in giving the shape of the equilibrium curve, on which the pressure varies only slightly, even if the absolute value of the pressure is somewhat high.

The last set of determinations on April 6 and 18 were with still another coil, a comparatively new one, but one which had been sufficiently seasoned. This coil gave readings consistent with the previous values on the I–III and II–V curves, and gave the same shape for the curve as that found with the two previous coils. There seems to be no question but that these are the correct values.

This variety of ice was obtained by increasing the pressure on I at low temperatures. The temperatures used here ranged from —65° to —80°. At —80° it is possible to run as much as 1000 kgm. beyond the transition curve before the reaction begins to run. Even so far removed from equilibrium as this, the reaction runs slowly and never seems to run to completion. The table shows the discrepancies in the stationary pressures when approached from above and below. The other points on the curve were obtained with regularly increasing temperature after the lowest. The temperature was raised as high as —23° to get the last point. The succession of points found in this way lie on a curve running nearly linearly with increasing temperature and pressure up to about —35°, where it turns and proceeds upwards nearly vertically. This verifies the form found for the curve by Tammann. This curve as found by Tammann crossed his I–III curve. Tammann advances as an argument against there being a true triple point at the point of intersection the experimental fact that it was possible to start with II at low temperatures, to proceed along the equilibrium curve with increasing temperature across the I–III curve into the supposed region of stability of III, and then to retrace one's steps, following down the original curve into the region of II where the two curves I–III and II–III are unmistakably different. This possibility, surprising as it seems, was verified also by direct experiment. The points of April 6 at —40° and —53° on the I–II curve were separated by points at —32°.5 and —26°.5, which are in the supposed region of stability of III.

The whole mystery is cleared up by the discovery of the II–III equilibrium curve. It may be permitted to anticipate the results as they were found on this curve in so far as they are needed to explain the curious facts found on the I–II curve. In the first place, the existence of the II–III curve puts beyond question the fact that there are two varieties of ice, II and III. The point of intersection of the II–III curve with the I–II and the II–III curves is at —35°, the triple point. This point is also the point at which the change in direction of the supposed I–II curve was found. Above this point the modification II passes into the modification III. The absolute regularity with which this turning point was found, both here and by Tammann, is to be explained by the experimental fact that it is impossible to superheat II with respect to III. In the course of these experiments it has never been possible to carry II the slightest distance into the region of III, the reaction running as inevitably as the reaction from a solid to a liquid when the solid is heated to the melting point. Furthermore this reaction, when it does run, runs with great velocity, since the temperatures are sufficiently high. The change is furthermore accompanied by a comparatively small change of volume. This evidently accounts for the curve having been overlooked by Tammann. The supposed crossing of the two curves I–II and I–III found by Tammann is to be explained by slight errors in the pressure measurements. The greatest difference between the curves is 30 kgm. This is the second bit of evidence alluded to on p. 482, that Tammann's absolute pressure measurements may be in error. The turning point of the curve found by Tammann is at the same temperature as that found here, —35°. The impossibility of superheating II also explains Tammann's inability to find points on the II–L curve. Apparently it is impossible to reach this. II appears to be surrounded on all sides by other solid phases.

The behavior of III with respect to II is not the reverse of II with respect to III. It is possible to subcool III greatly with respect to II. The amount of subcooling possible depends on a variety of factors. One of the most important of these is the interval of time which has elapsed since the water had previously existed in the form II. It is a fact verified repeatedly on all the other curves as well as on this particular one, that it is very much easier to obtain a phase after it has once been present in the apparatus. Thus it is possible to subcool III at least as far as —70° with respect to II, provided that II has never been formed. But if II has been formed previously, the reaction from III to II is very likely to run on passing from the III to the II region. This explains why it is possible to move up along the II–I curve, pass to the I–III curve, and then on decreasing temperature pass again to the I–III curve.

The points obtained experimentally have been classified with these facts in view. The points of March 25, 29, and April 5 obtained at temperatures above —35° after coming from lower temperatures on the I–II curve have been listed on the I–III curve in the tables.

The points are plotted in Figure 9. These points are the mean of the points found with increasing and decreasing pressures at temperatures very close to each other. Within the limits of error the points lie on a straight line. The two lowest points are irregular because of the extreme slowness of the reaction. It is interesting to notice that the line as drawn is heading straight for the absolute zero, the equilibrium pressure becoming zero at this temperature. Because of the slowness of the reaction it would be well nigh impossible to verify this conjecture experimentally. Except for the constant pressure error already mentioned, the curve as found by Tammann is of approximately the same shape as that found here. These figures give a drop in the equilibrium pressure of 360 kgm. between —40° and —80°, whereas Tammann gives 340 kgm. Tammann does not draw the line as straight, however, but prefers to make it slightly concave toward the temperature axis. This would bring the equilibrium temperature at atmospheric pressure up somewhat higher than the absolute zero.

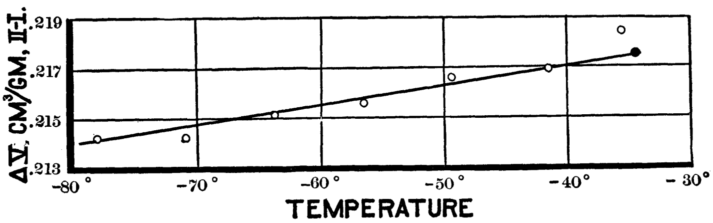

FIGURE 14. The change of volume when II passes to I.

The changes of volume, found by the method already described, are given in Table XIV., and shown graphically in Figure 14. Because of the fairly large difference in slope between the equilibrium curve and the lines of equal volume, the actual cycles described in measuring ΔV did not have the exact location shown in Figure 8. The lower parts of both DE and GF, which were fairly close together, projected over the equilibrium line into the region of stability of II. The upper end of the line CB was managed so as to just clear reaching into the region of I. This evidently introduces no essential error, since the compressibility and dilatation of one phase do not change on passing into the region of another. The difference merely means a somewhat wider extrapolation to determine the displacement on the equilibrium curve corresponding to the phase II, but this disadvantage is offset by the fact that what was an extrapolation for the phase I has now become an interpolation.

The change of volume is seen to be linear with temperature (or pressure) within a maximum error of 1/2 per cent. Only one point, that at —35.7°, shows a discrepancy as much as this, the average departure from linearity being in the neighborhood of 1/8 per cent.

Tammann gives three values for the change of volume which he lists as I–II, and two values listed as I–III. One of the supposed I–II values is above —35°, however, so that this must now be tabulated as I–III. He finds for I–II at —76°, 0.171 cm.^{3}/gm., and at —55°, 0.180. These values are considerably lower than the values found here. Tammann appears to have overlooked entirely the correction for the thermal dilatation of the fluid transmitting pressure; the effect of applying this correction would be to bring his values still lower. Tammann's results do agree with the present ones in showing an increase in the change of volume at higher temperatures, but Tammann finds a rate of increase

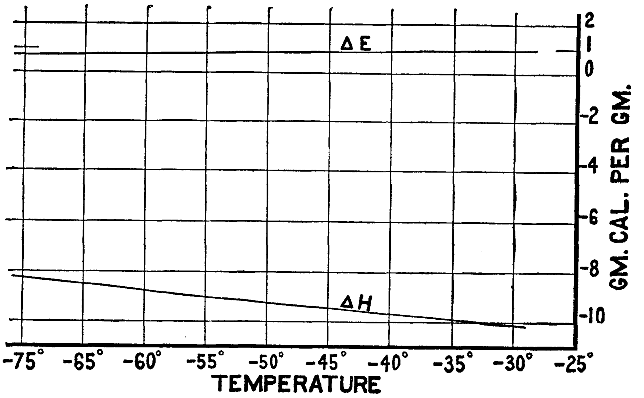

Figure 15. The latent heat and the change of internal energy when I passes to II.

TABLE XV.

Latent Heat, etc., on Equilibrium Curve Ice I–Ice II.

Temp. C.°.	Pressure, kgm./cm.^{2}.	Δv. cm.^{3}/gm.	$\frac{dp}{dt}$.	$p\Delta V$. gm. cal./gm.	ΔH. gm. cal./gm.	ΔE. gm. cal./gm.
−75	1794	0.2146	8.35	9.02	−8.31	0.71
−65	1886	.2154	8.35	9.52	−8.77	0.75
−55	1980	.2162	8.35	10.03	−9.22	0.81
−45	2072	.2170	8.35	10.54	−9.68	0.86
−35	2164	.2177	8.35	11.06	−10.15	0.91

four times that found here. Tammann states concerning his own data that his temperature coefficient is in all probability too high. His value at —33.5° for the supposed change I–II, but really for I–III, is 0.193 cm./gm. This agrees exactly with the value found here at the same temperature for the known change I–III, giving another bit of evidence from Tammann' s own data that above —35° II changes spontaneously to III. Tammann's value for the change I–III at —45° is 0.192, giving a temperature coefficient of the opposite sign from that found here. The actual values for the I–III change agree much better with the values found here than for the I–II change. The present values for I–III are 0.1904 at —32.5° and 0.2005 at —45°.

The data taken from these two curves needed in the calculation of ΔH and ΔE are shown in Table XV. and Figure 15. I gives out heat on passing to II and absorbs work. The work is greater than the heat, so that the internal energy increases on passing from I to II.

THE CURVE II–III.

This has been already stated to have been the curve overlooked by Tammann, but demanded thermodynamically. The discovery of it places beyond question the essential difference between the two varieties of ice II and III. The change of volume on this curve is very slight, so that it is easy to overlook it altogether, as did Tammann. A special method had to be used here in determining these equilibrium points. It is the reverse of the usual method. The usual method consists in changing the piston displacement and so the pressure at constant temperature. Change of phase is indicated by change of displacement with constant pressure. In the modification of the method used here, the displacement is kept constant and the temperature changed. The resulting change of pressure is plotted as a function of the temperature. Change of phase, accompanied by a slight change of volume, is indicated by a discontinuity in the direction of the temperature-pressure line.

At any given temperature during this change of phase there is only one corresponding pressure, the equilibrium pressure, unlike the former method, where the piston displacement may have any value within a considerable range corresponding to the same pressure and temperature. The change of volume is so slight that the interval of discontinuity in the direction of the temperature-pressure line extended over only 1° and 100 kgm. The method was made practicable by two things, the smallness of the containing cylinder, resulting in a very rapid attainment of temperature equilibrium, and the fact already noted, that it is impossible to superheat II with respect to III. Evidently if it had been necessary to superheat II even a single degree in order to start the reaction, the change of volume would not have been sufficient to carry the pressure automatically back to the equilibrium value, and the reaction would have run to completion.

The procedure in getting the points was to start with II at some pressure and temperature below the equilibrium line, and to raise the temperature by small intervals. Arrival at the equilibrium line was shown by an abnormally large rise of pressure. This pressure and the corresponding temperature gave one point on the equilibrium line. The reaction was not allowed to run to completion, because of the difficulty of recovering II after it has once been changed to III, but the pressure was immediately raised from the equilibrium pressure, bringing the material back into the region of stability of II, and causing the reverse reaction III–II to run to completion. Another equilibrium point was then found starting with this higher pressure.

The job was a rather fussy one because of the narrowness of the critical temperature interval. The temperature had to be maintained by dropping solid CO_2 into the Dewar flask, and some little practice was necessary before satisfactory results were obtained. Determinations of the curve were made on three occasions. The first two sets confirm the last set, but sufficient adeptness had not yet been attained with the method, and the points were discarded.

The final points, four in number, are shown in Table XVI. and Figure 9. The curve rises with increasing pressure from lower to higher temperature and is convex upward; it is terminated at either end by triple points, at the lower end by the point I–II–III, and at the upper end by the point II–III–V. This curve is new; there are no previous results with which to compare it.

The change of volume determinations were made also with a slightly modified method. The usual method of measuring piston displacement at constant temperature would have been available if the measurements had been made with decreasing pressure from the region of II to that of III, but the method was undesirable practically for two reasons. There was the difficulty of maintaining the temperature in the Dewar flask constant for a sufficiently long interval of time by hand, and there was the necessity of running down to the very lowest temperatures in order to recover II for the next determination after the reaction to III had been allowed to run to completion. This would have required much time and would have been very wasteful of solid CO_2.

The method used was a modification of that used in finding the I–II and the I–III points, namely, measurement of pressure as a function of temperature at constant displacement. The changes II–III and II–V were measured at the same time, so that some anticipation is necessary in describing the method. The diagram (Figure 16) illustrates sufficiently the paths described. The start was made at the point A with the phase II. The approximately vertical lines show the paths at constant displacement on which the pressure, temperature, and displacement are all known. The dotted lines show the connecting paths on which it was not necessary to know these values. The result of describing all these paths is to give a knowledge of the displacement corresponding to any pressure and temperature in either the region of stability of II or III or V. The discontinuity of displacement on the three equilibrium curves can be found immediately, and so the change of volume. It is

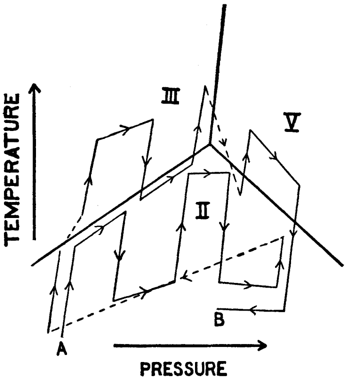

Figure 16. Shows the cycles described in finding the changes of volume II–III and II–V.

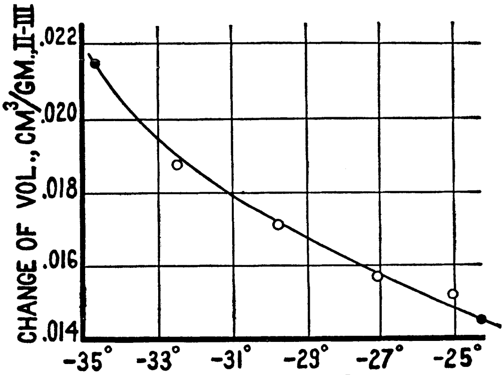

Figure 17. The change of volume when II passes to III.

to be noticed that the paths are described in such an order that one can easily apply the very small correction for wearing away of the packing or for viscous yield in the steel. The final point B is for the phase II. The diagram illustrates the impossibility of carrying II into the region of stability of either III or V, but the possibility of subcooling both III and V into the region of II.

TABLE XVI.

Data for the Equilibrium Curve Ice II–Ice III.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
April 19	−33.4	2290	
	−31.0	2580	
	−28.0	2910	
	−26.0	3220	
April 20		2400	0.0188
		2710	.0171
		3050	.0157
		3390	.0152

The experimental values of ΔV so found are given in Table XVI. and Figure 17. The actual volume of II is seen to be less than that of III. The percentage discrepancy of two of the points may rise as high as 2 per cent, but this means only a comparatively slight absolute error, less than 1 part in 2000 on the original volume. The ΔV curve is convex toward the temperature axis which is unusual.

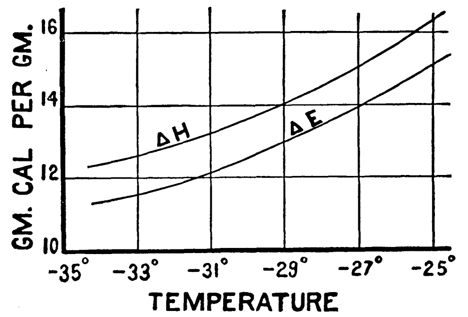

Figure 18. The latent heat and the change of internal energy when II passes to III.

The values for ΔH and ΔE deduced in the usual way are given in Table XVII. and Figure 18. III gives out heat on passing into II and absorbs work. But the mechanical work is comparatively small, so that the internal energy of II is less than that of III.

This completes the description of the equilibrium curves of the varieties of ice already known. This last curve had not been found before, and the rest of the curves to be described involve either one or two of the new varieties of ice found at higher pressures.

TABLE XVII.

LATENT HEAT, ETC., ON THE EQUILIBRIUM CURVE ICE II–ICE III.

Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm.	dp/dt.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$.
			From Curve.	Adjusted.			
−34.0	2230	0.0206	100	107	−1.08	12.4	11.3
−31.0	2530	.0179	125	130	−1.06	13.2	12.1
−28.0	2910	.0164	152	154	−1.12	14.5	13.4
−25.0	3370	.0148	184	189	−1.17	16.3	15.1

THE CURVE III–V.[10]

The points on this curve were usually obtained from above, coming from the region of stability of V into that of III. The reaction does not usually run of itself at temperatures above −25°; between −25° and −18° it is usually possible to reduce the pressure on V as far as the V–L curve, where V melts completely to water without the appearance of III. Below −25°, however, III is pretty certain to separate from V on passing slightly beyond the equilibrium curve. The points were usually obtained first at low temperatures and then at higher. Proceeding in this way it is easy to get the changes of volume also, although this did necessitate the reaction running to completion, because the reactions on this curve proved particularly sensitive to the previous appearance of the phase desired. If III and V had both been present recently, the reaction would run almost immediately, in either direction, at any temperature, on passing over the transition curve.

It has been already noticed that it is possible to carry both III and V down into the region of stability of II. Corresponding to this possibility we have the realization of the prolongation of the unstable curve III–V into the region of II. A point on this curve has been found at

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[10] For the notation V instead of IV for this new variety of ice, see p. 528.

—35°. The change in reaction velocity between III and V at different temperatures shows a greater and more striking change than that on any of the other curves. At the upper end, in the neighborhood of —20°, the velocity is explosive. It is possible to withdraw the piston by an amount corresponding to nearly the entire volume change of the reaction, and not be able to detect any change at all in the pressure, so rapidly does the change occur. While only 15° lower, at —35° the reaction runs so slowly that the attaining of complete equilibrium is a matter of several hours. This is the reason that the attempt was not made to prolong the equilibrium curve further. It is evident that we

TABLE XVIII.

DATA FOR THE EQUILIBRIUM CURVE ICE III–ICE V.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected Value.
Feb. 1	−25.05	3460	
	−24.20	3460	
	−23.00	3500	
	−21.50	3500	
	−20.30	3500	
	−18.35	3500	
Feb. 16	−25.25	3510	0.0541
	−22.80	3510	547
	−20.40	3520	546
	−18.40	3550	547
April 20	−22.1	3549	
	−19.4	3559	
	−24.4	3542	
	−29.0	3527	
	−35.3	3514	
	−23.0	....	.0570

have here something entirely different from the mechanism of ordinary chemical reactions which produces change of reaction velocity with temperature. For chemical reactions the temperature coefficient of velocity is almost universally in the neighborhood of 100 per cent for 10°, a value enormously lower than that found here.

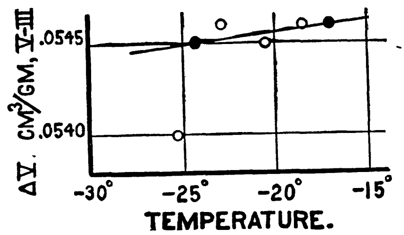

FIGURE. 19. The change of volume when V passes to III.

The actual determination of the equilibrium points was made on three occasions, February 1 and 16, and April 20. The first two were with the apparatus for the middle temperature range, that used with the mercury. These were made with the thermostat to keep the temperature constant. This apparatus was also used to give the changes of volume. The data of April 20 were taken with the low temperature apparatus. The particular object of this latter set was to obtain as accurately as possible the slope of the transformation curve, the previous data having shown that it was nearly vertical.

TABLE XIX.

LATENT HEAT, ETC., ON EQUILIBRIUM CURVE, ICE III–ICE V.

Temperature, C.°.	Pressure, kgm./cm.².	ΔV. cm.³/gm.	$\frac{dp}{dt}$.	$p\Delta V$. gm. cal./gm.	ΔH. gm. cal./gm.	ΔE. gm. cal./gm.
−35.0	3470	0.05446	2.75	4.43	−0.83	3.60
−30.0	3495	5454	2.75	4.46	−0.85	3.61
−25.0	3508	5461	2.75	4.49	−0.87	3.62
−20.0	3522	5469	2.75	4.51	−0.89	3.62

The equilibrium points are shown in Table XVIII. and Figure 9. The slope of the equilibrium curve is the slope given by the data of April 20, but the absolute value of the pressure as given by the mean of the other points is more likely to be correct. The equilibrium line is straight within the limits of error. The slope is in the same direction as for the curve I–II, but is less. There is no possibility of this line heading for the absolute zero.

The changes of volume, four in number and taken with the mercury apparatus, are given in Table XVIII. and Figure 19. The change is constant so far as could be judged from the points themselves, but the best values at the triple points would demand a slight decrease of this volume with decreasing temperature. In addition to the four points listed above, there is a fifth determination on April 20 by the method described on p. 495. This is higher by 4 per cent (0.2 per cent of the original volume) than the previous point. In view of the fact that the first four points very approximately satisfy the requirements at the triple points, there seems little doubt that they are the correct ones.

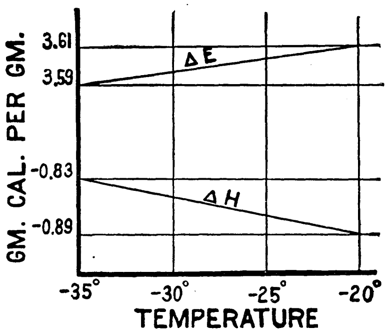

Figure 20. The latent heat and the change of internal energy when III passes to V.

The values of ΔH and ΔE calculated from these data are given in Table XIX. and Figure 20. III gives out heat on passing into V and absorbs work. The heat is very small, much less than the work, resulting in an increase of internal energy on passing from III to V.

The Curve II–V.

This curve has some of the properties of the II–III curve. It is characterized by small change of volume and by the fact that II passes into V immediately when the temperature is raised beyond the curve. The method of determining the points was the same as that of the II–III points. This was the last of all the equilibrium curves to be obtained. It was found after sufficient skill had been attained with the method, so that it was necessary to obtain the points only once. For this reason, the observation that it was impossible to heat II into the region of V was not tested by so many trials as the corresponding change II–III, and has therefore not quite so much probability of being absolutely true. The reaction velocity on this curve drops very much faster than it does on the II–III curve with decreasing temperature. This might, at lower temperatures, result in the apparent possibility of bringing II into the region of V, even if the reaction were actually running. This slowness of reaction makes very difficult the determination of the equilibrium points at the low temperatures, the determination being difficult enough anyway, because of the small change of volume. It would probably not be possible to extend this curve to very much lower temperatures than are given here. In partial explanation of the difference in the behavior of the reaction velocity with temperature on the two curves II–III and II–V, it is to be noticed that on the latter curve decreasing temperature is accompanied by increasing pressure, which of itself would tend to slow the reaction because of increasing viscosity, whereas on the former curve the retarding effect of decreasing temperature is offset by the accelerating effect of decreasing pressure.

TABLE XX.

Data for the Equilibrium Curve Ice II–Ice V.

Date, 1911.	Temperature, C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
April 19	−34.00	4200	
	−30.50	3970	
	−27.7	3800	
	−25.8	3650	
April 20		3700	0.0408
		4000	406
		4280	398

The equilibrium points, four in number, are given in Table XX. and Figure 9. These points lie on a straight line, the temperature rising with falling pressure.

The change of volume points, obtained by the method already described for the II–III curve, are shown in Table XX. and Figure 21. The change is sensibly constant on this curve. This means that the relation between compressibility and dilatation is such that the changes of temperature and pressure on the equilibrium curve produce the same change of volume in both II and V.

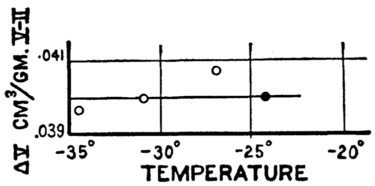

Figure 21. The change of volume when V passes to II.

The values of ΔH and ΔE, computed from these data, are given in Table XXI. and Figure 22. II absorbs heat on passing to V and absorbs work. The internal energy of V is greater, therefore, than that of II.

TABLE XXI.

Latent Heat, etc., on the Equilibrium Curve, Ice II–Ice V.

Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	ΔV. $\frac{\text{cm.}^3}{\text{gm.}}$.	dp/dt.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$,
			From Curve.	Adjusted.			
−34.0	4200	0.0401	75.6	68.4	3.95	12.4	16.4
−31.0	4010	401	69.8	68.4	3.77	13.9	17.8
−28.0	3800	401	62.4	68.4	3.57	15.1	18.7
−25.0	3570	401	55.0	68.4	3.36	15.9	19.2

The Curve V–L.

V was the second variety of ice found in this present work, the first being that stable at higher pressures, namely VI. It seems worth while to give here a short account of the actual order of the experiments, as it illustrates well the capricious character of these reactions. Ice V was first found at —8°. An experiment was being run on the change of volume of ice VI when passing to water. Pressure was being decreased; it had passed over the equilibrium pressure and a sufficient interval of time had elapsed to allow the pressure to automatically restore itself to the equilibrium value. The change to V occurred without warning. By good fortune, a reading at the bridge was being made at the particular instant, so that the entire

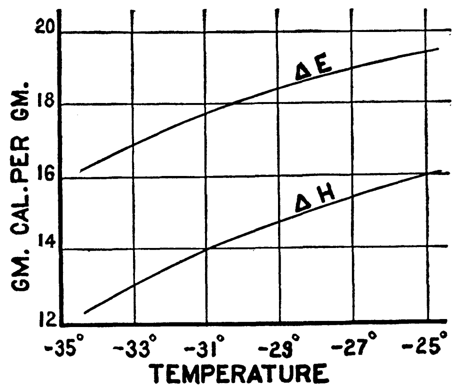

Figure 22. The latent heat and the change of internal energy when II passes to V.

process was observed. There was a sudden increase of pressure, followed by a slow fall past the equilibrium value VI–L to a final stationary value several hundred atmospheres lower down. This second stationary pressure had all the properties of a new equilibrium pressure, since the pressure was automatically restored to this value after withdrawal of the piston. After sufficient withdrawal of the piston, the pressure dropped in the normal way. The explanation, in view of the facts as they now appear with the complete diagram before one, is that ice VI at —8° was unstable. It had partly melted when it flashed suddenly into V with increase of volume and increase of pressure. The form V now found itself in the presence of water beyond the equilibrium curve. The water froze to V with decrease of pressure back to the equilibrium curve V–L. At the time, however, this explanation was adopted with considerable hesitation. No experience had been had of the very high reaction velocity possible between solids. After this set of readings, pressure was left at 2000 kgm. over night, the temperature gradually rising.

The next morning another run was made at —6°. The liquid froze to VI at —6° perfectly properly, with no trace of V. Pressure was increased considerably beyond the equilibrium value at —6° and then decreased. On the way down a new transformation point was found at pressures higher than either the VI–L curve or the supposed V–L curve. The new reaction ran with unusual velocity, equilibrium being attained in the time usually required for temperature equilibrium. On decreasing pressure further, the VI curve was passed over without incident, but a new equilibrium pressure was found lower down on the prolongation of the probable V–L curve of the day before. The explanation suggested itself that the upper transformation point was on the V–VI curve, the lower on the V–L curve. Some slight irregularities in the data made it desirable to dismount the apparatus after this run. During these experiments, the water had been enclosed in a glass bulb, as this was one of the series of experiments to detect if possible any effect of the transmitting liquid on the water. The glass bulb was found crushed to fragments, evidently because of the reaction between two solid phases with sudden increase of volume.

In the apparatus as set up next time, the glass bulb was discarded, therefore, and the water placed directly in a shell of copper. With this apparatus no trace whatever could be found of the new phase V. Measurements were made on the equilibrium and change of volume VI–L to temperatures as low as —20°. Lower temperatures could not be easily attained because of the trouble with the $CaCl_2$ cooling arrangements. The subject was then dropped for a couple of months;

in the meantime the data required for the mercury paper were finished.

On taking the matter up again, the only difference that presented itself between the two runs, one giving V and the other not, was that in the former run water had been in the presence of glass. The apparatus as set up again was made to differ from the former set up, therefore, only in the fact that splinters of Jena chemical glass were placed in the water, which was again included in a copper shell. The very first attempt at —10° was successful. Pressure was increased beyond the VI–L line, the reaction VI–L had started, and the equilibrium pressure had been reached, when the phase V put in an appearance, displacing VI. Briefly, the mere addition or subtraction of the fragments of glass appeared to be the determining factor. When it was desired to work on VI in the subcooled region, the glass was omitted; when V was desired, the glass was added. Even then the appearance of V was under surprising conditions. V was never formed directly out of the water, but always in the presence of the phase VI. Furthermore, V showed a preference for appearing only when VI, water, and glass were present together, usually during determinations of the equilibrium pressure VI–water, either during increasing or decreasing pressure. The facility with which V might replace VI was the source of some annoyance. Once a day's work was lost because V had successfully come in without being noticed. V might, however, form directly from the solid VI, as described above. All this holds only for the initial appearance of V, it being very much easier, as already explained, to produce it after it had appeared once. It was possible in this way to get V to separate directly from the liquid, if it had appeared recently before.

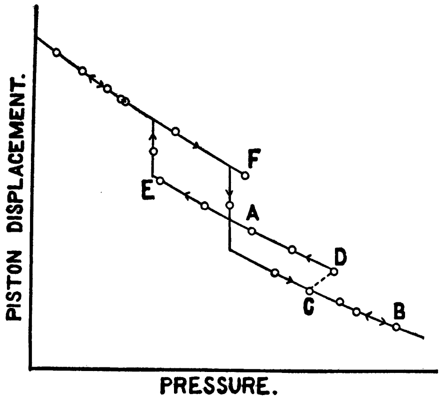

Figure 23. Shows the way in which V may appear. The dotted line C–D indicates the sudden transition from VI to V.

Figure 23, plotting piston displacement against pressure, shows well the way in which V might appear. With increasing pressure, the water froze regularly to VI, as shown at A. The point F shows the possibility of subcooling the water before the reaction starts. The pressure was then increased on the phase VI to the point B without incident. On decreasing pressure beyond C, VI suddenly changed to V with increase of pressure to D. This change took place so far beyond

TABLE XXII.

Data for the Equilibrium Curve Ice V–Water.

Date, 1910.	Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
Nov. 11	−7.8	4860	0.0541
14	−6.0	5200	0512
19	−8.9	4140(?)	
1911			
Jan. 30	−10.1	4490	0702
	−18.75	3420	
	−16.65	3680	
	−11.00	4440	
Jan. 31	−14.5	3910	
	− 4.0	....	0578
Feb. 2	−20.6	3050	
3	− 2.0	5940	0552
4	−13.1	4030	0747
8	−15.45	3770	0765
	− 9.50	4600	0693
9	− 7.17	5010	0623
	− 4.3	5480	0586
	− 0.88	6120	
11	− 7.65	4890	0636
	− 4.60	5420	0587
	− 1.40	6020	0519
13	−10.8	4480	0693
	−10.5	4460	0663
	−14.2	3900	0724
14	−17.65	3460	0790
	−20.80	3040	0839
	−14.32	3780	0753
22	− 1.60	6040	0543

the equilibrium line that the change of volume VI–V was not sufficient to raise the pressure to the equilibrium value VI–V. From D, pressure was regularly reduced to E, the melting point of V. Beyond E, the curve of increasing pressure was retraced.

These remarks about the manner of appearance of V hold only for temperatures above —25°. At lower temperatures, V may be made to separate from the solid phases III or II without the presence of glass. In any event, V was the hardest of any of the solid forms to obtain, the only certain way being via II, which demanded lowering the apparatus to below —60°.

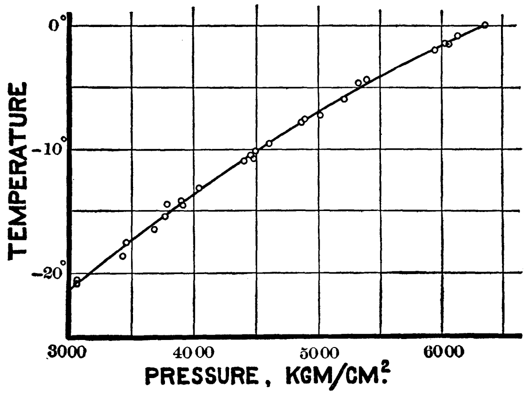

Figure 24. The freezing curve V–L.

The actual determination of the points on the V–L curve was made with the apparatus for the middle temperature range, temperature being kept constant as usual with a thermostat. The equilibrium points are shown in Table XXII. and plotted in Figure 24. As is seen, these points were obtained on a large number of occasions, with different pressure measuring coils, and with nearly all possible combinations of all the pieces of apparatus ever used with this general type of apparatus, part after part being replaced as it was destroyed by explosion. The lower part of the equilibrium line is a trifle high, still passing through a number of points, but not through the mean of all the points. This was demanded in order to obtain consistent values for the latent heat at the triple point L–III–V, the slope of the upper end of the III–L curve being extraordinarily sensitive to small changes, as already explained. The curve as given does not differ by over 0.2° from the best curve through the points for V–L alone. The curve as given extends to —21°, 4° into the region of stability of III. It is known, however, that it is possible to extend the curve as far as —25°. On one occasion a point was found here, but it is not sufficiently accurate to plot, owing to defective temperature control. The behavior at the upper end of the V–L curve is the exact opposite of that at the lower end. It was not found possible to prolong the equilibrium curve of V and L the slightest distance into the region of stability of VI, V always passing spontaneously into VI. This was tried several times; the reaction runs if the penetration into the VI region is even as slight as 1°.

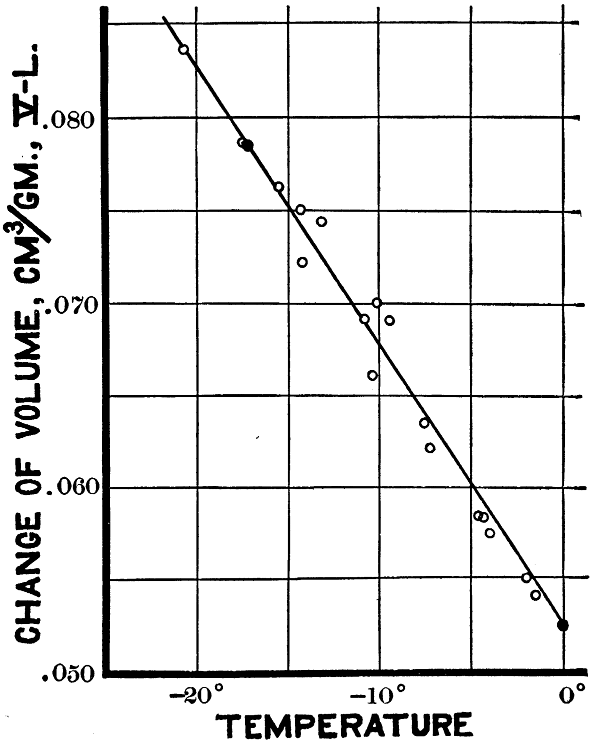

Figure 25. The change of volume when V passes to the liquid.

More or less trouble was found in determining the change of volume. When kerosene was used as the transmitting fluid, there seems to be some action below 0°, either between the water or the ice and the kerosene. This results in a slight rounding off of the corners of the displacement-pressure curve, so that the actual discontinuity is difficult to determine. This would point to a solution of the water in the kerosene. The rounding off of the corners is not enough to affect appreciably the equilibrium pressure. The effect was on the whole less marked when gasolene was used as the transmitting fluid. The change of volume points are given in the same table with the equilibrium points and also in Figure 25. All the data before February 10 were obtained with kerosene as the transmitting fluid; gasolene was used for the results obtained afterwards. The gasolene points are on the whole better, although the difference here is not sufficient to have necessitated the use of gasolene instead of kerosene. The changes of volume VI–L are much more affected by the transmitting fluid, below zero, than are the changes V–L. The first two values of November 11 and 14 are not plotted, since the design of the apparatus in the first few attempts was not good. Small portions of the water were likely to separate from the rest after a single freezing, so that unless the pressure was carried considerably beyond the freezing pressure, part of the water was likely to remain liquid, giving too low an apparent change of volume. The lowness of these first two points is to be explained in this way.

TABLE XXIII.

LATENT HEAT, ETC., ON THE EQUILIBRIUM CURVE, ICE V–WATER.

Temp. C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	ΔV. $\frac{\text{cm.}^3}{\text{gm.}}$.	$\frac{dp}{dt}$.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$.
			From Curve.	Adjusted.			
−20.0	3140	0.0828	123	123	−6.10	60.5	54.4
−15.0	3800	754	140	139	−6.72	63.4	56.7
−10.0	4510	679	160	157	−7.18	65.9	58.7
− 5.0	5440	603	184	180	−7.69	68.1	60.4
− 0.0	6360	527	210	208	−7.85	70.0	62.2

Within the limits of error, the relation between temperature and change of volume is linear. The lower end of the curve is about 1 per cent higher than what would be demanded by the points themselves. This was made necessary by the conditions at the critical point.

The values of ΔH and ΔE found from these data are given in Table XXIII. and Figure 26. Water gives out heat on passing into V, and absorbs work. The work is very much less than the heat, so that the internal energy of V is less than that of the liquid.

The Curve V–VI.

This is the last of the curves of equilibrium between two solid phases. The manner in which the curve was first found has been already described. The characteristics of this curve are the same as those of the other solid-solid curves; very high reaction velocity at the upper end, with enormously retarded reaction velocity at the lower temperatures. The slowing of the reaction was so great as to make impracticable the determination of points lower than —25°. Anomalous results obtained once or twice are to be explained by the slowness of the reaction velocity. The nature of the anomaly is shown in Figure 27, plotting piston displacement against pressure. It is as if there were two discontinuities, at A and B, and so two transition points. The explanation is probably as follows. The reaction from VI to V starts at the upper end of the steel shell. This reaction runs with increase of volume, so that the layer of the new ice V may form a protecting layer over the remainder of the old ice VI below. This protecting layer is capable of standing some appreciable stress at this high pressure and low temperature, so that changes of hydrostatic pressure do not reach the nest of

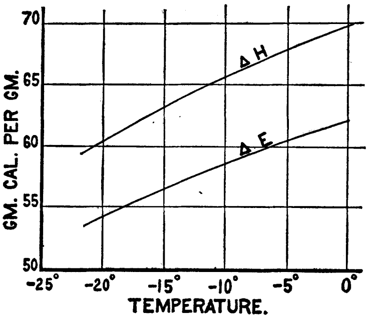

Figure 26. The latent heat and the change of internal energy when V passes to the liquid.

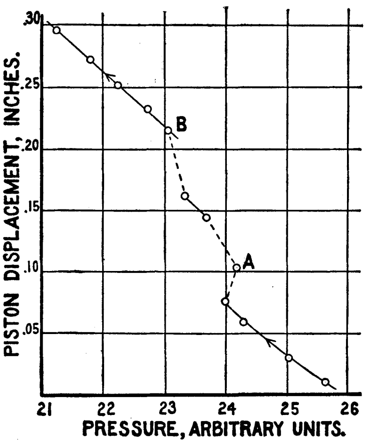

Figure 27. False equilibrium at low temperatures on the V–VI curve, due to the slowness of the reaction and the viscosity of the solids.

ice VI below, until the pressure has been reduced by an amount corresponding to the strength of the ice V. An exactly similar effect was found once on the III–V curve at —25°. That the ice in passing from one solid to another is capable of exerting considerable stress is shown by the occasional rupture of the steel shells containing the water.

TABLE XXIV.

DATA FOR THE EQUILIBRIUM CURVE, ICE V–ICE VI.

Date, 1911.	Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm. Corrected.
Jan. 30	−10.10		0.0396
31	−14.5	6360	378
	− 4.1		400
Feb. 1	−16.60	6320	346
3	−18.1	6380	
	−24.65	6320	
	−22.70	6360	
	−19.90	6370	
	−12.05	6370	
	−12.08	6380	383
	− 2.00	6380	
4	−13.1	6360	396
20	−19.7	6360	386
	−16.8	6370	384
	−13.9	6370	384
21	−11.25	6370	386
22	− 8.15	6390	380
	− 5.00	6380	387
	− 1.60	6380	386

These were 9/16 inch o. d. and about 3/64 inch thickness of wall. In fact, it seems rather surprising that the effect did not prove troublesome on more than these two occasions.

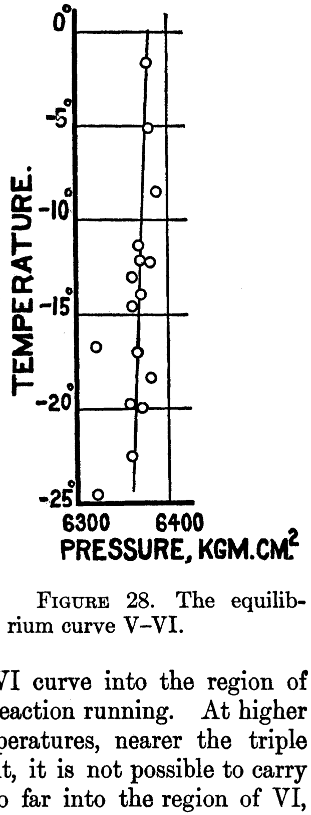

FIGURE 28. The equilibrium curve V–VI.

The regular apparatus for the middle temperature range was used in finding these points. Some skill in manipulation was necessary to arrive on the curve at all. The procedure was to start with the water impregnated with glass splinters and raise the pressure at a temperature somewhere between —10° and —20°. On sufficiently overpassing the unstable VI–L curve, VI would separate out. After some little while V would appear. With the first signs of its appearance, indicated by a rise of pressure, the pressure was increased as rapidly as possible, in a few seconds, to the V–VI curve, where the automatic change of volume was sufficient to ensure retaining of the equilibrium pressure after freezing of the remaining mass of liquid. This method of procedure was made necessary by the fact that at the temperatures at which it is easy to obtain V, it is possible to pass from either side of the V–VI curve into the region of instability on the other side, without the reaction running. At higher temperatures, nearer the triple point, it is not possible to carry V so far into the region of VI, corresponding to the fact already noted that at the triple point itself it is impossible to carry V any distance at all into the region of VI.

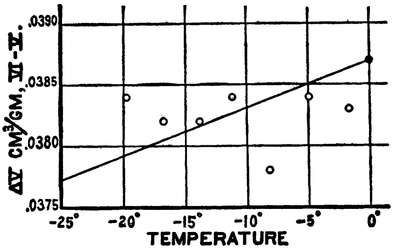

FIGURE 29. The change of volume when VI passes to V.

The equilibrium pressures and temperatures are shown in Table XXIV. and Figure 28. The equilibrium line is nearly at constant pressure, but there is an unmistakable though slight increase of pressure at the higher temperatures. Within the limits of error, the equilibrium curve is a straight line.

The change of volume points, obtained by the usual method of observing the piston displacement at constant temperature, are given in Table XXIV. and Figure 29, plotted on a very much enlarged scale.

TABLE XXV.

Latent Heat, etc., for the Equilibrium Curve, Ice V–Ice VI.

Temperature, C.°.	Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	ΔV. $\frac{\text{cm.}^3}{\text{gm.}}$.	$\frac{dp}{dt}$.	$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$.	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$.
−20.0	6365	0.03809	.80	5.682	−0.181	5.50
−15.0	6370	3828	.80	5.716	−0.185	5.53
−10.0	6374	3847	.80	5.748	−0.190	5.55
− 5.0	6377	3866	.80	5.779	−0.195	5.58
0.0	6381	3886	.80	5.812	−0.199	5.61

Here again the points found before February 10 with kerosene as the transmitting fluid show much less regularity than the points obtained afterward with gasolene. The kerosene points have been omitted from the diagram. The effect may be due in part to the increased viscosity of the kerosene under pressure. Within the limits of error, the relation between V and temperature is linear, the change becoming less at lower temperatures as one would expect.

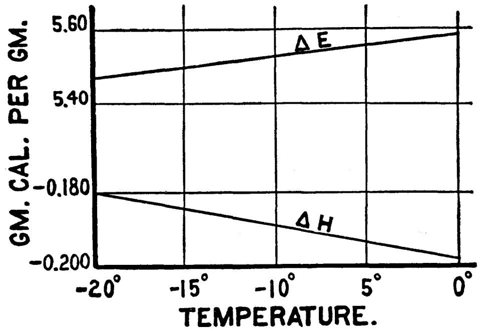

Figure 30. The latent heat and the change of internal energy when V passes to VI.

The missing triple point, mentioned at the beginning, is evidently given by the intersection of this line, V–VI, with the line II–V. This point is apparently situated at about —65° and 6300 kgm. Evidently the reaction velocity will be so slow at these temperatures and pressures that it would be hopeless to try to reach it. The missing equilibrium curve starting from this point is evidently II–VI. There is even less chance of realizing this than of getting down to the triple point, always assuming of course that some new variety of ice does not appear.

The values of the latent heat and the change of energy calculated in the usual way from the data are given in Table XXV. and Figure 30. The latent heat, owing to the approximate perpendicularity of the equilibrium curve, is almost vanishingly small. V gives out heat on passing to VI, but absorbs work. The heat is almost negligible compared with the work, so that the internal energy of VI is greater than that of V by nearly the amount of this work.

The Curve VI–L.

This modification of ice was the first one discovered in the present work, and has engaged more attention than any of the other forms. It has been studied over a pressure range of more than 16,000 kgm., nearly three times the pressure range of all the other modifications put together. So far as can be judged, this is the final form of the solid. This ice shows characteristics in its behavior different from any of the others, characteristics which are particularly significant for the theory of the solid-liquid states. In fact, this is the only modification stable over a pressure range wide enough to indicate what may be expected at still higher pressures, as yet unreached.

The manner in which this variety of ice was first found in the course of the measurements of compressibility has been already described in the introduction. The appearence of this ice resulted simply in an irregular disturbance at the upper end of the compressibility curve. It was evidently impossible to make any accurate measurements by this method of the freezing pressure or of the change of volume. All that could be stated about the freezing pressure was that it was less than a certain value, the maximum pressure reached during a run when there was a disturbance, and all that was known about the change of volume was that it was higher than a certain value, the discontinuity in the compressibility curve. The lower and upper limits so set on these quantities were found to be consistent with the more accurate values found later.

At the time that these disturbances were found no great confidence was felt in the explanation that the effect was really due to the freezing of the water. All of the compressibility measurements were made in the presence of mercury. Now it had been already found that mercury freezes under pressure, and at pressures very close to those actually found. At 0°, for instance, the freezing pressures of water and mercury, according to the final accurate determinations, are about 6400 and 7600 kgm. respectively, and these two transitions seemed much closer together in the preliminary work because it was necessary to superpress the water considerably before freezing begins, while the superpressure required for mercury is very small. It is true that there were very great quantitative difficulties in the way of supposing the effect due to the freezing of the mercury, but still the neighborhood of the mercury freezing point produced a sensation of disquietude.

In order to definitely rule out the possibility of complications from the neighborhood of the freezing point of mercury, a form of experiment was devised in which there was no mercury present. This was the experiment also briefly alluded to in the introduction on the electrolytic conductivity of water. The water was placed in a shell of steel or glass, and the conductivity measured between two concentric brass cylinders attached to the insulating plug and suspended in the water. The pressure chamber was filled with kerosene by which pressure was transmitted directly to the water. There was no mercury anywhere about it. The water was not absolutely pure, ordinary tap water being used, which was sufficiently conducting for the purpose. In one case distilled water with 1/10 per cent HCl was used. The resistance was measured with a Kohlrausch bridge and a telephone in the usual way. At high pressures there was unmistakable evidence of some sort of change. The electrolytic resistance at first decreased with rising pressure, passed through a flat minimum, rose slowly, and then very rapidly to several times the former value, the rapidity being such as to be almost equivalent to a discontinuity. This pressure of sudden rise was taken as the freezing pressure, since it would be natural to suspect the solid incapable of conducting. The pressure of transition was measured in this way at several temperatures. In all, three sets of readings were made with different forms of apparatus, and the last one six months after the first. In the last determination, the existence of the effect independent of the mercury having been already established, the water was enclosed in glass with a mercury seal, the more effectively to prevent absorption of impurities from the kerosene. The three sets of determinations gave perfectly consistent results. A brief statement as to the existence of a new variety of ice as proved by these experiments was published in the Physical Review, vol. 31, 1910, p. 606. The values as found by these measurements lie on a straight line, and agree with the possible limits found with the compressibility measurements, except that at the highest temperature, 22°, freezing had once been found to take place during the compressibility measurements at a pressure lower than that found here. This was disconcerting.

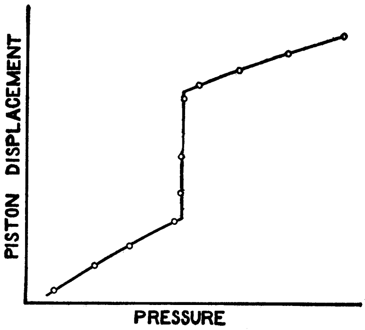

FIGURE 31. Shows the sharp change of volume during freezing.

The transition curve as found in this way did not give all the information needed for a complete statement of all the quantities involved in the change. A complete statement thermodynamically could be made if it were possible to measure also the change of volume during the change. This seemed at first sight of doubtful possibility. Tammann had made such measurements up to 2000 kgm., but had not been able to go much higher because of leak. As it was, even at 2000, a correction had to be applied for the leak, which was furthermore made as small as possible by the use of a heavy oil, such as castor oil. In the present work it was necessary to go to many times this pressure, the equilibrium pressure even at 0° being 6400 kgm. The difficulty was furthermore increased by the necessity for using some very light and mobile oil to transmit pressure, the castor oil freezing absolutely solid under such pressures as were to be used here. It was felt, therefore, to be a real step when it was found that the packing used in the previous high pressure work was entirely satisfactory when used for this purpose. It is possible with it to retain liquids as mobile as ether, CS_2, pentane, or mercury, absolutely without leak, up to the highest pressures attainable. Measurements of the change of volume have been made up to 15,500 kgm., and this limit was set by yield of the steel cylinders and not by failure of the packing. The readings of the piston obtained were consistent to a few ten thousandths of an inch. The only troublesome effect found with the packing was a slight wearing away by abrasion, owing to the enormous friction. This effect was troublesome only over a wide pressure range; for the limited motion of the piston during freezing or melting the effect was negligible.

It was also a part of the preliminary work to show that the freezing is sufficiently sharp to give trustworthy measurements of the change of volume. The presence of impurity in the water will be shown by a rounding off of the corners of the melting curve and by a change in the value of the equilibrium pressure with the relative proportions of liquid and solid present. Figure 31, chosen at random from the earlier measurements, shows the sharpness of freezing and the consequent freedom from impurity. In the majority of subsequent measurements, the question of absence of impurity having been settled, it was customary to find only one value for the equilibrium pressure, corresponding to a mixture varying from one third to two thirds liquid.

The equilibrium points obtained by the change of volume method were found to be consistently lower than the supposed transition points found by the method of change of resistance. There can be no question whatever but that the change of volume points are the correct ones. The cause of the discrepancy probably is the formation of the eutectic mixture of ice and salt.

Measurements made with the electrolytic conductivity method after the completion of the rest of the experiments, with the new apparatus giving also the piston displacements, showed that the flat minimum in the conductivity curve previously referred to occurs at nearly the pressure of the beginning of freezing. Evidently at first pure ice separates out, leaving the remaining liquid richer in whatever salt produces the conductivity. The total quantity of this salt remains nearly constant, but its concentration and so its association are increasing, so that on the whole we have a decrease in the conducting power. When the pressure has been carried so far that the concentration reaches the eutectic value, the solid salt separates out with the pure ice and we have the sudden jump in the resistance. That this was the case was also suggested by a fact observed once or twice when using water in glass with a mercury seal. This was that the sudden discontinuity might be either a short circuit or an open circuit. Evidently the short circuit is due to the penetration of the mercury through the mass of ice along the core left by the freezing of the pure ice to the walls of the tube.

The points on the VI–L curve were obtained with two different pieces of apparatus. The points between —20° and 20° were found with the apparatus already described as used for the middle temperature range. For the higher pressures, up to 20,500 kgm., another form was used. The particular point of weakness in the middle temperature apparatus is the connecting tube. The new form for the highest pressures was made in one piece, therefore. This has been already described as the third piece of apparatus. It is to be noticed that with this there is no correction necessary for the thermal dilatation of the transmitting fluid. These measurements to the highest pressures were made after the completion of all the others. It was confidently expected to find a new variety of ice, but none was found.

The pressure measurements with the high pressure apparatus were made in the usual way by measuring the resistance of a coil of manganin wire. This had been calibrated by comparison with an absolute gauge up to 13,000 kgm., which was about the limit of the gauge. The pressures above this were obtained by a linear extrapolation, therefore. There does not seem much danger in doing this in view of the fact that the relation is linear within 1/10 per cent up to 13,000.

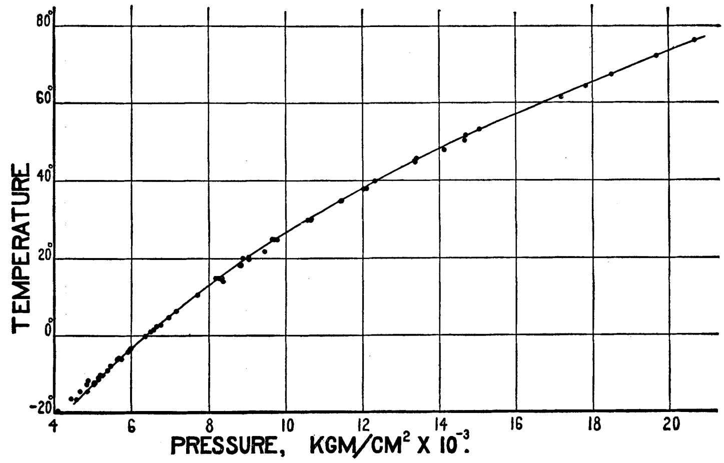

Figure 32. The freezing-curve VI–L.

For the middle temperature range the high pressure apparatus offers the advantage of fewer connections over that actually used. There are practical difficulties in the way of its use below 0°, however. It is necessary to submerge the entire lower end of the hydraulic press with the cylinder into the constant temperature bath. There is considerable flow of heat out of the bath along the heavy connecting bars of the press. It would for this reason have been difficult and expensive to have maintained temperatures below zero with the $CaCl_2$ solution. Points have, however, been obtained with the high pressure apparatus over the entire range above zero.

The equilibrium points are given in Table XXVI. and Figure 32. A greater variety of groupings of apparatus have been used for the points

TABLE XXVI.

DATA FOR THE EQUILIBRIUM CURVE ICE VI–WATER.

Date, 1910.	Temp. C.°.	Pressure, kgm./cm.².	ΔV. cm.³/gm. Corrected.	Date, 1911.	Temp. C.°.	Pressure, kgm. cm.².	ΔV. cm.³/gm. Corrected.
Oct. 7	0.0	6380+	0.0914	8	0.0	6360+	916
		6360−	0915			6360−	906
8	0.0	6360+	908	9	1.05	6500	
		6340−	908		2.55	6660	
12	6.4	7170+	876	March 3	−3.4	5970	908
		7150−	880		−6.2	5630	943
15	14.0	8380+		4	− 3.2	5990	923
18	15.0	8360+			− 9.2		955
19	14.80	8330+	798		−12.2	5040	1014
		8310	798	6	−10.4	5280	981
24	2194	9470+	712		−11.3	5160	971
		9450−	710		−12.5	5030	963
25	18.4	8840+	776		−14.5	4870	978
Nov. 3	18.42	8800−	758	April 28	30.0	10660	
4	10.63	7710+	878		38.2	12120	
		7710−	842		45.2	13360	
	2.90	6770−	903	May 8	30.2	10680	0.0593
5	4.78	6960−	888	9	38.0	12040	556
	1.65	6580	911		45.8	13410	
11	0.0	6360	916		53.4	15050	
	− 7.8	5470		13	38.4	12120	618
14	− 4.0	5910			48.0	14140	541
	− 4.2	5910	938		55.5	15670	566
17	−11.7	4890	853		61.6	17200	
18	−16.5	4440	900		67.5	18500	
	−19.6	4100	936	25	35.0	11450	647
19	0.0	6370	914		30.0	10590	671
	− 8.9	5390	994		25.0	9790	713
	− 6.0	5630±	931+	26	25.0	9680	705
			959−		20.5	9050	758
21	−12.2	5080+	1035		15.0	8260	795
		5050−	1004		0.0	6350	928
22	−10.9	5160+	959	29	0.0	6360	902
Jan. 28		5130−	916		15.1	8180	797
1911.	− 5.7	5690+	997		20.1	8890	754
		5690−	914	30	25.1	9650	707
30	−10.1	5200	1044		30.1	10450	676
	− 6.0	5750+		31	35.0	11470	629
		5740−			40.0	12330	590
31	−14.5	4680			45.0	13380	512
Feb. 1	−16.60	4590		June 1	45.0	13380	563
2	−12.75	4850		13	51.8	14700	516
7	0.0	6340+	932		64.30	17840	
		6350−	895		72.15	19670	
					76.35	20670	

on this curve than for any other. It was on this curve, for instance, that the test was made of the possibility of interaction between water and the substances in contact with it. The water was used in steel or copper or glass vessels, in contact with kerosene or gasolene or mercury. No difference in the equilibrium pressures could be found with any of these different forms of apparatus, but below zero it did seem desirable to use gasolene instead of kerosene. Figure 31 shows piston displacement aaainst pressure for one of the points on this line. The corners of the curve were seldom more rounded than here. The pressure measurements on this curve were made with six different manganin coils.

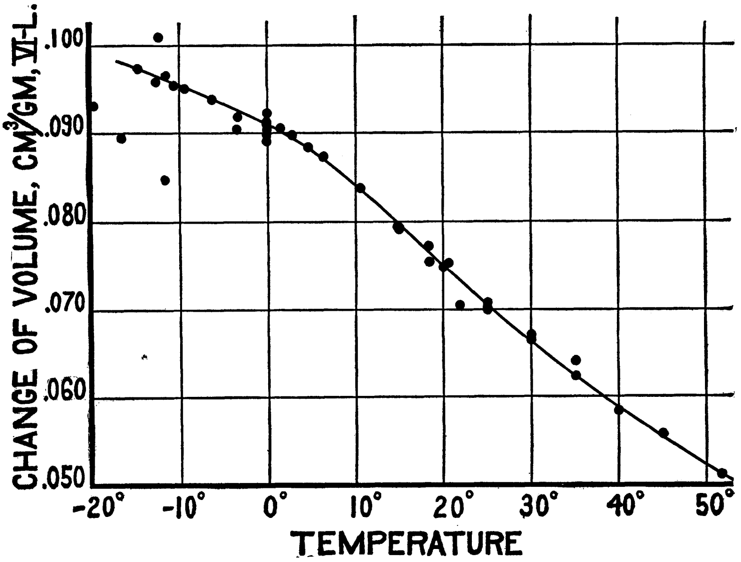

Figure 33. The change of volume when VI passes to the liquid.

Figure 32 shows that the equilibrium curve runs perfectly smoothly, without incident of any kind, from the lowest temperature of the sub-cooled region, —17°, to the highest temperature and pressure, 76° and 20,500 kgm. The curve is convex upward, like all the other curves of equilibrium between the liquid and the other solid forms of water. Attention is called to the five bad points lying off the equilibrium curve at the lower end.

The change of volume is shown in the same table with the equilibrium points, and graphically in Figure 33. All the values that were ever obtained have been given in the table, but not all these are plotted. In the earlier work, ΔV was found both during freezing and melting, that is, with increasing and decreasing pressure. In the paper on mercury a detailed discussion is given, showing why the values found during decreasing pressure are very likely to be in error. None of these values are plotted. When it has not been specifically stated in the table, the value has been obtained during decreasing pressure. Furthermore, all the points obtained with the kerosene as the transmitting fluid below 0° have been discarded from the figure, with the exception of the three low points to be mentioned later. Nearly all the other points found with the kerosene below zero lie above the curve given.

At the highest pressures there is an entirely new source of error which justifies the discarding of certain points. Before the explanation was found, considerable trouble was given by the points apparently lying on two distinct parallel curves. A succession of points on the low curve, not very regular, was first found, reaching up to 55°. The pressure was then pushed to 18,500 for an equilibrium point, and then after that, more change of volume points were found at lower pressures. These all lay on the high curve. Some of these points were determined three times with different fillings of the apparatus, giving almost identical results, and the measurements were extended back to 0° to compare with the results with the other piece of apparatus, giving approximate agreement here also. The high curve was then followed out again to higher temperatures, giving good points until at 45° the value jumped again to the low curve. The possibility of a new kind of ice was ruled out by the regularity of equilibrium points. Explanation was found in the viscous yield of the steel. This has the curious property of going on at a uniform rate during the time occupied by an experiment, not being asymptotic as one might expect. This yield had been carefully looked for at the lower pressures and not found. During the long course of the experiments so much practice had been obtained that during these last measurements the readings of pressure and piston displacement were made with almost clock-like regularity every six minutes. The yield was so slow as to be imperceptible during that interval of time, and the readings were made with such regularity that the effect was not discovered, as it otherwise would have been, by irregular points on the curve. Once the effect was discovered, it was found entirely competent to account for all observed discrepancies, since the melting occupies a fairly long time, between one and two hours. Another point at 45° was then found, applying a correction for the yield by noting its rate during the half hour before and after change of state. This corrected point lay consistently with the others on the high curve. Evidently the succession of high points found at the same pressures, as well as the previous low points, is to be explained by the seasoning effect of the maximum pressure of 18,500, which was applied between the two sets. The last low point is due to the passing to the viscous state again, after the seasoning effect had disappeared in time or had been overcome by too high a pressure. After the point at 45° another point was found at 52°, applying the correction for yield, and found to lie on the high curve consistently with the others. It did not seem worth while to attempt points at still higher pressures, because the correction becomes more difficult to apply at the high pressures, both because the yield is becoming more rapid, and because the yield does not remain uniform in time at the highest pressures.

TABLE XXVII.

Latent Heat, etc., on Equilibrium Curve Ice VI–Water.

Temp. C.°.	Pressure, kgm./cm.^{2}.	ΔV. cm.^{3}/gm.	*dp/dt*.		$p\Delta V$. $\frac{\text{gm. cal.}}{\text{gm.}}$	ΔH. $\frac{\text{gm. cal.}}{\text{gm.}}$	ΔE. $\frac{\text{gm. cal.}}{\text{gm.}}$
			From Curve.	Adjusted.			
−15.0	4790	0.0980	100.5	99.6	10.99	59.0	48.0
−10.0	5280	960	106.2	106.5	11.87	63.0	51.1
− 5.0	5810	938	112.4	113.8	12.77	67.1	54.3
0.0	6360	916	118.8	120.0	13.66	70.4	56.7
+ 5.0	7000	884	125.1	125.8	14.51	72.5	58.0
10.0	7640	844	132.0	132.7	15.13	74.4	59.3
15.0	8310	798	140.0	140.0	15.56	75.5	59.9
20.0	9000	751	148.3	148.5	15.84	76.6	60.8
30.0	10590	663	167.3	167.3	16.45	78.8	62.3
40.0	12390	590	189.0	188.7	17.14	81.7	64.6
50.0	14430	523	213.7	215.4	17.69	85.3	67.6
60.0	16690	477	243.0	242.9	18.68	90.5	71.8

The behavior of this cylinder is interesting from the point of view of elasticity. It shows the impossibility of obtaining perfect elasticity very much beyond the original elastic limit. This cylinder had been previously seasoned for use in this work by subjecting it for some hours to 28,000 kgm. The hole was then bored out from the original 7/16 inch to 1/2 inch. The 28,000 kgm. had produced a stretching at the inside from 7/16 inch to perhaps 15/32 inch. Even this high pressure did not completely do away with viscous yield at pressures as low as 10,500. Another interesting feature is the approximate constancy of the rate of yield over a pressure range of 5000 kgm., from 10,500 to 15,500, as shown by the fact that the low points are nearly all the same distance below the corresponding high points. This, too, bears out an observation made before, that elastic after-effects, hysteresis, yield, etc., are greater in larger masses of metal. This cylinder was 4 1/2 inches o. d. and 1/2 inch i. d. No such viscous yield was found in the cylinder with which the change of volume of mercury was measured up to 11,000. This cylinder was 3 inches o. d. and 9/16 inch i. d., and had been previously subjected to 24,000 kgm.

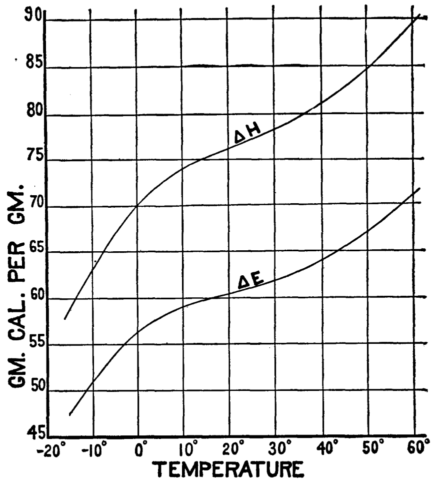

FIGURE 34. The latent heat and the change of internal energy when VI passes to the liquid.

In view of this yield, therefore, the values at the higher pressures which were evidently affected by this yield have not been included in the figure. The curve connecting ΔV with the temperature has a point of inflection, which is not shown by any of the other curves. This is of significance, as will be seen.

The values of ΔH and ΔE found in the ordinary way are shown in Table XXVII. and Figure 34. The point of inflection in both these curves is the particularly interesting feature. Water on passing to VI gives out heat and absorbs work. The work is less than the heat, so that the internal energy of VI is less than that of the liquid.

The data obtained with the high-pressure apparatus may be used to determine one other quantity which the other apparatus could not give, that is, the difference of compressibility between solid and liquid. This may evidently be found from the difference of slope above and below the melting point of the curves connecting piston displacement with pressure. If everything had been ideally perfect the other apparatus should have given it too, but the quantity to be determined is very small, and the irregularities introduced by the transmitting liquid passing from one vessel to another at a different temperature, which might not be perfectly constant, were so great as not to admit of any results of value. With the high-pressure cylinder, everything is in one piece, and there are fewer complications. The values obtained even with this are very irregular, but they are given as having some value in pointing out the direction of the effect at high pressures. The points are shown with sufficient accuracy in Figure 35. This shows a very rapid decrease in the difference of compressibility at high temperatures and pressures.

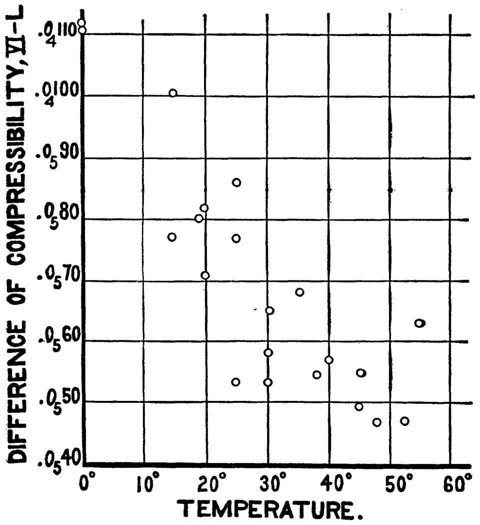

FIGURE 35. Showing the directly determined values for the difference of compressibility between VI and the liquid at various equilibrium temperatures.

This completes the presentation of the actual data. The points were determined separately, those on one equilibrium curve being independent of those on another. But the curves drawn through the points, particularly those for the latent heat and the change of volume, have not been in all cases the best curves through the points of the single equilibrium curves in question, but have been influenced by the behavior of the two neighboring curves meeting at the triple point. Some discussion of the way in which these data were adjusted at the triple points seems called for.

TABLE XXVIII.

The Co-ordinates and Change of Volume at the Triple Points.

Point.	Temp. C°.	Pressure, kgm./cm.².	ΔV. cm.³/gm.		
III-L-I	−22.0	2115	III-L 0.0466 (461)	L-I 0.1352	III-I 0.1818 (.1823)
II-III-I	−34.7	2170	II-III 0.0215 (208)	III-I 0.1963 (.1958)	II-I 0.2178
V-III-L	−17.0	3530	V-III 0.0547	III-L 0.0241	V-L 0.0788
V-II-III	−24.3	3510	V-II 0.0401 (408)	II-III 0.0145	V-III 0.0546
VI-V-L	+ 0.16	6380	VI-V 0.0389 (388)	V-L 0.0527 (522)	VI-L 0.0916

The Triple Points.

The equilibrium curves themselves were in all cases, except one, accurate enough so that the three curves met at the triple point naturally, without the slightest forcing. The one exception is the lower end of the V–L curve, already mentioned, where it seemed desirable to raise the lower end by 0°.2. Even this curve as thus raised is not actually inconsistent with the data. The values of the co-ordinates of the triple points are shown in Table XXVIII.

In selecting the best values for the change of volume, the greatest weight was attached to the curve which was evidently most self-consistent. The values on the other two curves were then so adjusted as to give consistent results with the least violence possible. The full details of the process are shown in the table, which gives the final values, and in parentheses the values found from the individual curves before this process of adjustment. The signs are so chosen that the change of volume is an increase when the reaction runs in the direction in which the symbols read. At every point, the sum of the two smaller changes is equal to the larger.

An adjustment was necessary in seven out of thirteen possibilities. The average adjustment was about 5 parts in 10,000; the maximum, 7 parts in 10,000 of the original volume. The points on the III–L curve were so difficult to obtain, as already explained, that the entire course of this curve was in large measure determined by the behavior at the two triple points at either end.

With regard to the values for the latent heat and the change of internal energy, there was room for more difference of opinion as to the best way of making the adjustment. The latent heat, given by the formula $\Delta H = T\Delta v \frac{dp}{dt}$, is seen to depend on the change of volume, already fixed, and on the slope of the equilibrium curve. The slope was determined graphically from the equilibrium curves. There is chance for considerable error here, and the possibility of introducing comparatively large changes into ΔH by a very slight raising or lowering of the equilibrium curve, too slight in all cases except that of III–L mentioned to introduce a perceptible change in the co-ordinates of the triple point. On the equilibrium curves solid-solid, which run approximately vertically, the latent heat is usually so small as to have very little effect in the adjustment. It was possible to determine this latent heat with a fair degree of accuracy, however, and so this was left without adjustment, the other values being adjusted so as to be consistent with it.

Evidently when the values of the latent heat are properly adjusted, the values of the internal energy will also be consistent, because these differ from the latent heat only by a quantity involving the change of volume, which is already consistent at the triple point.

The tables already given, under the equilibrium curves separately, enable an estimate to be formed of the amount of adjustment necessary. Two values are listed both for $\frac{dp}{dt}$ and ΔH. The first value of $\frac{dp}{dt}$ was obtained directly by graphical construction from the equilibrium curves, and from this the first value of ΔH was calculated directly, point by point. The final value given for ΔH is the value taken from smooth curves so drawn as to check at the triple points. From this final value of ΔH the final value of $\frac{dp}{dt}$ was calculated, and listed in the column of final values. Table XXIX. gives the values of ΔH at the triple points. The III-L curve is the only one that it was necessary to juggle with in any way, and this has already been explained. The symbols are so chosen that heat is absorbed when the reaction runs in the direction in which the symbols read. Thus, the heat I–L is given as 79.8. This means that heat is absorbed when I passes to water.

The changes of internal energy at the triple points are also given in Table XXIX. The positive sign means that the reaction runs in the direction indicated with increase of internal energy.

TABLE XXIX.

Latent Heat and Internal Energy at the Triple Points.

Point.	ΔH gm. cal./gm. (in the first lines). ΔE gm. cal./gm. (in the second lines).					
III-L-I	III-L	50.9 48.6	L-I	−56.1 −62.8	III-I	− 5.2 −14.2
II-III-I	II-III	12.3 11.2	III-I	− 2.2 −12.2	II-I	10.1 − 1.0
V-III-L	V-III	0.9 − 3.6	III-L	61.4 59.5	V-L	62.3 55.9
V-II-III	V-II	−16.0 −19.3	II-III	16.9 15.7	V-III	0.9 − 3.6
VI-V-L	VI-V	0.2 − 5.6	V-L	70.1 62.4	VI-L	70.3 56.8

There are several considerations of interest in connection with the diagram that are not directly concerned with the data as given. These are the questions as to our knowledge that these forms are actually solid, as to the possibility of other forms of ice, the possibility of existence of any form out of its region of stability, and the question of reaction velocity.

Are the Various Forms Really Solid?

This is the first question that naturally presents itself as to this work. The experimental evidence so far has merely been that there is a discontinuous change of volume; the new modifications have not been seen; it is impossible to take the pressure off and examine them, because they are unstable; why then are we justified in assuming that they are solids and not liquids? No direct evidence on this point has been collected in this work; the improbability of their being anything except solids seems so great as to make needless the special arrangement of apparatus necessary to give a direct proof. This was doubly needless, since Tammann has already given direct proof that II and III are solid.

The most striking evidence of Tammann is for III. Tammann cooled a steel cylinder containing ice III to the temperature of liquid air, then released the pressure and took ice III out and examined it. The temperature was so low that the reaction from III to I did not run immediately. III was solid and gradually changed to ice I with large increase of volume. In another experiment Tammann placed an electric contact maker in the water. Freezing to a solid was shown by the refusal of the contact maker to work, both for III and II.

That V and VI are also solid is made probable by two bits of evidence. In the first place, the reactions between V and III and V and VI are exactly similar to those between I and III and I and II. There is no mistaking the difference between a reaction solid-solid and liquid-solid. In the second place, when the reaction VI–V runs with increase of volume, the containing vessel, whether a glass bulb or a fairly heavy metal cylinder, may easily be destroyed. In this reaction V has the larger volume. It, then, must be solid, and probably VI also.

The possible crystalline forms of the different modifications seem to be impossible of direct observation. It would be possible to insert windows in the apparatus and look at all the forms, but this would probably give no information whatever. On several occasions the apparatus was opened and the cylinder of ice I, which had frozen under pressure, was removed. This was always a perfectly structureless, translucent mass, capable of giving no information whatever as to any of its crystalline properties.

OTHER POSSIBLE FORMS OF ICE.

In a recent paper Tammann[11] has stated the probable existence of a fourth variety of ice, very much like ordinary ice in its properties. The evidence for this was very meagre. Slight discrepancies found on the equilibrium curve I–L could be explained by it; also a momentary rise of pressure on one occasion after the fall of pressure proper to melting had begun. Seven successive attempts of Tammann to get the same effect again failed. It is evident that the discrepancies on the I–L curve might be due to pressure errors; a new manometer used by Tammann gave pressures 50 kgm. lower than the former one, and we have already seen that the crossing of the I–III and the I–II curves found by Tammann must be set down to pressure errors. Finally, Tammann states that ice IV may separate out from water when cooled to −7°. The fact that there is a different modification is shown by placing the ice so formed in a dilatometer, and warming slowly. At −2° there is a sudden increase of volume of about 1/10 per cent, followed by regular increase of volume and melting at 0°. The ice IV appears, therefore, to have a slightly less volume than ice I. In this experiment, sufficient attention does not seem to have been paid to the possibility of there being internal strains in the ice. It seems plausible that the water, freezing suddenly as it must at −7°, might so freeze as to produce a slight volume compression. On increasing temperature, this strain is relieved by the softening of the ice in the neighborhood of the melting point. This weakening of the ice near the melting point has been established by experiment. At high pressures it is undoubtedly true that internal strains may produce anomalous effects, as was found on at least two occasions.

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[11] Tammann, ZS. Phys. Chem., **72**, 609–631 (1910).

Entirely apart from Tammann, however, there is independent experimental evidence of the possibility of two forms of ice, differing in density by 1/10 per cent, the amount found by Tammann. Two modern experimenters, Nichols[12] and Vincent,[13] as well as several previous observers, have each found that the density of ice may have either one of two distinct values. The difference seems to be connected with the manner of formation of the ice, whether natural or artificial. The natural ice, when kept for some time, tends to assume the value for the artificial ice. Barnes,[14] however, failed to verify the work of Nichols, and the most recent work of Leduc suggests that the discrepancies may possibly be due to dissolved air.

The question is as yet unsettled, with the probability, however, that the ice does not exist. In order to leave open the possibility of the establishment of its existence, however, the numeral IV has been reserved for this according to Tammann, and the first of the two new varieties found in this paper has been called V.

Besides this, there have appeared from time to time spasmodic notices concerning ice existing in crystalline forms other than the hexagonal. This is usually natural ice, which has been subjected to intense cold in the far north. None of these statements seem to have been subsequently verified, however.

In the course of the present work evidence was obtained as to the possibility of the existence of another form at high pressures. It seems probable that the five discrepant points found on the lower end of the VI–L curve may be due to the presence of some other form of ice than VI. These points were obtained on two separate occasions more than two months apart. Every one of the equilibrium points which have ever been obtained has been plotted in the diagrams, except a few where the temperature control was defective, and which have been mentioned. There are nowhere any points lying so far off the curve as these five. It seems hardly probable that the five worst points should have all been bunched in the same place, all lying consistently on a new curve. The probability of there being a new kind of ice is strengthened by the change of volume measurements made at these same points. These points are shown on Figure 33 for the change of volume VI–L. They lie far below the smooth curve, further than even the wildest of the discarded points, and they also lie consistently on another curve. The probability seems very strong for another modification of ice. This modification, if it does exist, is unstable in the locality found, V being a more stable form. Whether this new form has any region of stability at all is open to question; there is no necessity for it.

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[12] Nichols, Phys. Rev., **8** (Jan., 1899).

[13] Vincent, loc. cit.

[14] Barnes, Trans. Roy. Soc. Canada, **3**, Sect. III, 3–27 (1909), and Phys. Rev. (July, 1901).

Whether there are still other forms stable at the highest pressures is of course a matter of pure conjecture. No inconsistencies were ever found suggesting in any way the existence of another form in the region studied. The domain of stability of ice VI as found is already five times more extensive than that of any of the other modifications. Furthermore, the course of the freezing curve and of the change of volume curve is such that both of these curves could be extended without difficulty to infinite pressures and temperatures. VI seems at any rate suited to be a final modification.

In this connection, some comment seems called for as to the possibility of predicting new forms. Of course it is well known that there is no such possibility from the equations of thermodynamics alone; the domain of existence of any form may be extended indefinitely in either direction without running into thermodynamic inconsistencies. But every substance, besides satisfying the identical relations of thermodynamics, also satisfies its own particular characteristic equation. This characteristic equation is determined by the special internal mechanism of the substance in question. It seems *a priori* possible that the approach of a new form should be heralded by some change in the mechanism, which should have its effect on the characteristic equation. But no such effect as this has been noticed. One substance may be extended across the boundary line into the unstable region beyond, with no appreciable change in either the compressibility or the dilatation, the two quantities determining the characteristic equation. And on an equilibrium line, the neighborhood of a triple point does not cast its shadow before, either by a change in the direction of the equilibrium line, or of the change of volume line, or of the curves of latent heat or internal energy. So far as the data presented in this paper are concerned, there seems to be no way of making the prediction. Nevertheless the conviction remains that if one had a complete description of the internal mechanism, it would be possible to find some criterion as to the possible stability of other configurations. What additional data are needed to give a sufficient knowledge of the mechanism? The question is an interesting one for investigation.

THE POSSIBILITY OF SUBCOOLING OR SUPERHEATING.

The facts regarding this subject have nearly all been mentioned incidentally in the course of the detailed description of the experiments. Although no observations of the possibility of subcooling or superheating were made separately for their own sake, yet the observations collected incidentally on this subject are nearly as numerous as all the other observations together. The effect was of course observed during every measurement of a change of volume, and frequently on other occasions. It was likely to be a very troublesome effect, preventing the appearance of the modification desired, so that at least sufficient familiarity had to be obtained with the slight regularities shown by the apparently confused mass of facts so that the modification of ice desired could be forced to appear.

First with regard to the solid phases. It has been found possible to go across nearly every one of the boundary lines into the region of instability on the other side. I has been found in the region of III and II; II in that of I (at low temperatures); III in that of I, II, and V; V in that of III, II, and VI; and VI in that of V. The only excursion of this kind which has not been found possible is that of II into the region of III or V. This latter reaction always ran immediately on passing the slightest amount into the neighboring country. For the other reactions no fixed limits could be set to the extent by which it was possible to overstep the boundary. The amount depends on the size and shape of the vessel, on the materials in contact with the ice, on the element of time, and on caprice. In general, however, the limits became narrower at high temperatures, as one would expect.

With regard to the passing from the solid to the liquid, the experience here is but a verification of the experience of everybody else; that it is impossible to superheat a crystalline phase with respect to the liquid. No good reason for this has ever been given, but no exception has ever been found, and it is coming to be regarded as a law of nature. One would think that if there were ever a chance to find an exception it would be here, where the materials are made viscous by the high pressure, and where the reaction must run with increase of volume against the pressure, doing considerable external work.

On the other hand, it is the easiest possible matter to subcool the liquid with respect to any one of the four solid phases bordering on the domain of the liquid. In fact, it is often a matter of some difficulty to start the reaction liquid-solid, superpressures of 1500 or 2000 kgm. being sometimes necessary. The amount of superpressure or subcooling necessary to start the reaction is again a matter of caprice. On the VI–L curve, however, where the greatest range was open to observation, there seemed to be in general a tendency for the subcooling to increase at high pressures.

In consequence of the possibility of carrying one phase into the region of another, it is possible to prolong certain of the equilibrium lines beyond the triple point into the region of instability beyond, thus realizing equilibrium points between two unstable phases. The equilibrium lines which have thus been extended are: I–L into the region of II, III–L into the region of I (by Tammann, not in the present work), III–L into the region of V, I–III into the region of II, III–V into the region of II, and VI–L into the region of V. It may also be possible to extend II–III into the region of I, although this was not tried. The only curves which it was found experimentally impossible to extend were II–III into V, II–V into III, and V–L into VI. There seems to be no obvious generalization about the possibility of extending these curves; everything seems to depend on the particular character of the substances in question. There was one plausible generalization from only two instances, which was missed by a very narrow margin, namely that it is impossible to extend a melting curve at the upper end into the region of another solid. The attempt always failed on the V–L curve, and until the very last day failed on the III–L curve. On this very last day, when the change of volume points II–III–V were being found, it was desired to pass from III to V. The greatest difficulty was experienced in doing this. Pressure was increased on III at about $-20°$ to 4500, and the temperature then raised until III began to melt, thus spoiling the generalization. It was finally necessary to lower the temperature to $-40°$ before V appeared. It is therefore conceivable that there are circumstances when V–L might be extended into VI, or II raised into the region of III or V.

It may be mentioned that at every triple point there is at least one equilibrium line which it has not been found possible to cross. At four of the five triple points there are two such lines, and at the fifth, I–II–III, the possibility of carrying II into the region of I was not tried. At three of the five points water is one of the substances, so that the statement is obviously true; at the other two points the solid II has the same relation to the solids above it that the solids above have to the liquid above them.

It was not found possible to extend any two of the curves so far into a region of instability as to give a triple point between three unstable phases, nor was the third unstable curve starting from this unstable triple point ever found. This third curve would have no region of stability whatever. The nearest approach to this was in the extensions of the III–L and VI–L curves. No especial attempt was made to realize such an unstable triple point, however, as it would have been a matter of considerable difficulty, but there seems no reason why such a point should not be found.

No such constancy was ever found in these subcooling experiments as to suggest the necessity of the existence of the metastable limit, as is claimed by many writers. With a particular piece of apparatus it may be possible to obtain fairly consistent results, but when the apparatus is being continually changed as it was here there seems to be no obvious regularity. There is no reason why there should be, if the formation of the nucleus of the new phase, which starts the reaction, is a matter of chance as seems likely. Owing, however, to the fact that there is at every triple point one equilibrium curve which it is not possible to cross, there are going to be lines reaching from every one of the triple points limiting the existence of one or more of the phases, which give the same impression as the metastable lines recently drawn by Tammann in the neighborhood of the triple point I–III–L for water, and also in the neighborhood of a triple point of phenol.[15]

In one respect the possible amount of subcooling showed great regularity and is of sufficient significance to deserve special mention. This is the fact, already noted, that a form is much more likely to appear again if it has appeared recently before. This fact was of great convenience in obtaining the change of volume points, because here one phase has to be allowed to be completely replaced by another, and the first phase is then wanted again in obtaining the second ΔV point. Very little difficulty was experienced in getting the desired form to appear under these circumstances. This was particularly true on the V–VI and the V–L curves, the modification V being the hardest to obtain initially. On the V–L curve a succession of ΔV points was obtained without difficulty, V always putting in an appearance when desired, separating directly from the liquid with very little subcooling, although V was never obtained directly from the liquid the first time, but only by way of VI after considerable subcooling. This ability of V to separate directly from the water could be retained for several hours at points removed 1000 or 2000 kgm. from the equilibrium curve. The ability was once retained over night, pressure not being far removed from the equilibrium curve. The disposition to react depends both on the element of time and on the amount by which pressure has been changed from the equilibrium value. This predisposition to react is lost if a third modification has intervened. Thus, on the occasion mentioned, when III was melted at 4500 kgm. in the endeavor to obtain V, only a half hour previously the reaction II–V had been running in either direction with the greatest facility. The subsequent conversion of II into III resulted in the complete loss of disposition of V to appear.

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[15] Tammann, ZS. Phys. Chem., **75**, 75–80 (1910).

In explanation, there must be some structure in both the liquid and the solid not ordinarily accounted for, some nucleation or aggregation of the molecules left as a heritage from the previous modification, which is particularly adapted to fall back again into the old position. The possibility of such nuclei in the solid must show that the molecules in a crystal are not arranged in the absolutely symmetrical way usually thought of. The fact that these nuclei may persist for some time in the solid does not seem so surprising as the fact that they exist at all. For the liquid, the reverse is the case. The existence of nuclei might be expected; they are known to exist even in a gas, but that these nuclei may persist for some hours in an assemblage of molecules supposed to be in constant interchange with each other might not be expected at first. The disappearance of these nuclei is a matter of extraordinary slowness, considering the usual times involved in the motion of the molecules as a liquid. Doubtless the formation of these nuclei is intimately connected with the freezing of a liquid for the first time. The freezing can start only from one of these nuclei. The formation of one of these nuclei in an unimpregnated liquid is a matter of chance, and until the molecules do happen to fall together into the right position the freezing cannot start.

REACTION VELOCITY.

Here again no accurate measurements were made. The velocity depends on too many things to allow quantitative results of value without the expenditure of a great deal of time. These disturbing factors are such as the size and shape and material of the containing vessel, the rapidity of heat conduction, and the distance from the equilibrium line. But just as for the question of subcooling, so here, every measurement ever made, whether of the equilibrium pressure alone or of the change of volume, involved this matter of reaction velocity. One had to be sure before making a reading that the reaction had stopped running, and in the endeavor to waste no more time than was necessary the progress of the reaction was constantly watched, so as to make the reading as soon as possible after sensible equilibrium had been reached.

There are two distinct types of behavior of the reaction velocity, according as the reaction is between a solid and a liquid or between two solids. In general the reaction between solid and liquid was slower than between solid and solid. The time for the completion of the reaction liquid-solid was about two hours on the I–L, V–L, and lower end of the VI–L curve. No particular variation in this time was noticed from one end to the other of the I and V curves, but at the upper end of the VI–L curve, the velocity had been very appreciably accelerated, the time for completion of the reaction at the upper end being about one hour. On the III–L curve, as already mentioned, the reaction was very much slower. It was not practicable here to wait for the reaction to run to completion, but the equilibrium points were taken as the mean of values approached from above and below. This shows that the velocity depends on the form into which the water is transformed as well as on the heat of reaction, for the heat III–L is of the same magnitude as that of the neighboring modifications I and V. On all the curves the velocity seemed the same for melting as for freezing.

The most striking behavior of the reaction velocity is shown by the reaction solid-solid. The velocity ranges from explosive rapidity at the end near the triple point to such sluggishness 20° further down as to make further prolongation of the equilibrium curve out of the question. Of course the very low heat of reaction would lead one to expect, other things being equal, a high rate of transformation, but that the heat of reaction has practically nothing to do with it is shown by the enormous temperature coefficient of reaction velocity, while the heat of reaction is practically independent of temperature. The slowness of the reaction does not depend so much on the actual temperature as on the nearness of the triple point. Thus I–II is explosive at its triple point, −35°, while at −35° III–V is almost impossible; III–V is explosive at its own triple point, −17°, but at this temperature V–VI may take a couple of hours to run to completion.

The explanation does not suggest itself. The mere fact of such rapid reactions between solids is itself sufficiently surprising. It does not seem as if the mechanism could be the same as that of an ordinary chemical reaction. It is as if the molecules changed from one crystalline arrangement to another by snapping round on their axes, like the supposed molecular magnets of a piece of iron in a magnetic field. The high temperature effect is difficult to account for. Certainly no known viscosity effect has so high a temperature coefficient.

Some connection seems likely between this high velocity at the triple point and the impossibility of superheating a solid. There is no doubt but that at this point the molecules of the solid have a perfectly astounding possibility of motion. The passage to the liquid may still depend on the chance formation of nuclei in the solid, but the freedom of motion of the molecules in the solid may be so great as to secure the practically instantaneous formation of the proper grouping. This recalls the question proposed a few pages back as to the possibility of predicting the presence of a new phase from the behavior of a single other phase. Here we have a hint as to the possibility of predicting a third phase by an enormous reaction velocity between two others.

The Compressibility of the Different Forms of Ice.

These compressibilities have not, with one exception, been directly measured, but it is possible, nevertheless, to obtain some idea as to this magnitude for those varieties of ice which are anywhere in equilibrium with the liquid. This includes all the varieties except II. The compressibility of VI has been directly measured above 0°, and the initial compressibility of ice I has been computed. It has been already stated that the data do not possess the requisite accuracy to permit a direct determination of the compressibility of the other forms of ice. The approximate determination comes by finding the actual volume of the different kinds of ice along the equilibrium lines. The volume of water is known along these lines, and also the change of volume when the liquid passes into the solid, so that the actual volume of the solid may be obtained. This volume will change with temperature and pressure along the equilibrium line. The approximation to the compressibility is made by assuming that the change of volume due to changes in temperature along an equilibrium line is negligible compared with the change due to pressure. The error so introduced may be found at 0° for ice I at atmospheric pressure, where it is 3 per cent. Furthermore, at any point except in the immediate neighborhood of the origin, the thermal expansion of the ice is very probably less than that of the liquid with which it is in contact. This enables us to put an upper limit of 10 per cent as the probable error introduced by assuming all the change of volume along an equilibrium curve to be brought about by changes of pressure.

The complete values of the volume are shown in Table XXX., which gives the approximate compressibility along these curves. For comparison, the approximate compressibility of the water at the corresponding pressure and temperature is also given. In consequence of the change of volume due to temperature, the quantity listed as compressibility is too big on the ice I curve, and too small on the other curves which rise to higher temperatures with higher pressures. The compressibility of the ice is uniformly less than that of the water, as one would expect, varying from 1/3 to 2/3. On all the curves except the III–L curve, the compressibility shows a very marked decrease with rise of pressure, the decrease being more rapid proportionally for the liquid. The same decrease would probably also have been shown on the III–L curve, if it had been possible to make the measurements of the change of volume with greater accuracy. On the I–L curve, the change for a range of pressure of only 2000 kgm. is abnormally high. This might be accounted for by a negative temperature coefficient of expansion of ice at the lower end of the curve. The change of volume measurements I–III have already suggested this as a possibility. The change of compressibility with pressure is greatest at the low pressures, being particularly great in the region of instability of VI. In general, when one variety of ice replaces another, one would expect the new form stable at the higher pressures to show the lower compressibility, corresponding to the smaller volume; but this is certainly not true in the case V–VI, and probably not true when III replaces I. The compressibility of each modification seems to be a property inherent in that modification, depending probably on the symmetrical arrangement of molecules in the crystal, and not depending so directly on the volume.

As verifying these values very roughly, the directly determined difference of compressibility between L and VI has been shown in Figure 35. The values are evidently not of any great regularity. The only two points found below 15°, at 0°, are much too high. These would give a value for the compressibility at 0° of $.0_530$ as against $.0_56$ from the data above, $.0_56$ being too small. But in the region where the points are thicker, between 15° and 50°, the agreement is better, discrepancies being of the order of 0.0_51. These points run to higher pressures than the actual determinations of the compressibility of water, and do show strikingly the rapid decrease in the difference between the com-

TABLE XXX.

VOLUME AND APPROXIMATE COMPRESSIBILITY OF ICE ON EQUILIBRIUM CURVES.

Pressure, kgm./cm.².	Temp. C.°.	Vol. of Water cm.³/gm.	ΔV. cm.³/gm.	Vol. of Ice cm.³/gm.	Approx. Compressibility of Ice.	Compressibility of Water at Same Point.
Ice I–Water.						
0	0	1.0000	0.0900	1.0900	0.0_435	0.0_452
500	− 4.1	0.9777	0998	1.0775		
1000	− 8.7	9588	1096	1.0684	0_416	37
1500	−14.0	9414	1201	1.0615		
2000	−20.3	9253	1318	1.0571	0_58	29
Ice III–Water.						
2000	−22.5	0.9250	0.0476	0.8774	0.0_591	0.0_430
2500	−20.1	9099	373	8726		26
3000	−18.3	9874	286	8688		24
3500	−17.0	8867	231	8636		21
Ice V–Water.						
3500	−17.0	0.8870	0.0785	0.8085		
4000	−13.6	8781	733	8048	0.0_572	0.0_4190
4500	−10.1	8694	681	8013		
5000	− 7.0	8610	634	7976	53	164
5500	− 4.2	8543	590	7953		
6000	− 1.6	8478	549	7929	47	140
6500	+ 0.6	8418	516	7902		
Ice VI–Water.						
4500	−18.0	0.8689	0.0985	0.7705		
5000	−12.8	8604	968	7636	0.0_4102	0.0_4164
5500	− 7.7	8536	940	7596		
6000	− 3.2	8472	928	7544	0_572	140
6500	+ 1.1	8418	905	7513		
7000	5.0	8370	882	7488	55	126
8000	12.6	8271	816	7455	48	120
9000	19.5	8156	755	7401	43	110
10000	26.0	8055	697	7358	37	104

pressibility of water and VI with rising pressure. This point has some bearing on the discussion of the general nature of the change of state solid-liquid at high pressures.

DISCUSSION OF THE RESULTS.

So far in this paper merely the numerical results have been presented, without much discussion of their significance. For the liquid, the change of volume at different temperatures and pressures has been found, without discussing the shape of the p-v-t surface which these combine to give. For the solid states, the data have been presented for each variety of ice separately, without any consideration of the general features which may be common to all. The object of this discussion is to give a comprehensive survey of all the results, especially for the transition liquid-solid, and to point out the theoretical significance of these data at very high pressures.

For the liquid, the results will have their chief interest in showing how water passes from an abnormal liquid at low pressures to a normal one at high pressures. The data do not have so much suggestiveness for a theory of the liquid state as would those for some normal liquid, and in any case it would be dangerous to generalize from the behavior of a single substance, but the results at the higher pressures do suggest at least the nature of the effects to be expected in general at high pressures.

The results for the liquid at even temperature and pressure intervals have been collected in Table XXXI. In this table the smoothed results obtained separately above 0° and below 0° have been given without any attempt to smooth the values of either set so as to make connections with those of the other. But the fact that the two independent sets of determinations do run smoothly into each other makes probable the accuracy of the work. Above 7000 kgm. the value of the thermal dilatation used in computing the table was obtained by an extrapolation. This is probably good up to 10,000 kgm. in giving the actual volume at any temperature and pressure within the narrow range of existence of liquid water, but the use of the tables in any theoretical considerations demanding knowledge of the derivatives would be dangerous at the highest pressures. Above 3000 kgm., and indeed above 2000 kgm., the dilatation has been assumed to be independent of the temperature over the range of 22°, as has been sufficiently shown by the work of Amagat. For values below 2000 the variation of the dilatation as found by Amagat has been used in computing the table. Of course below 0° the variation of dilatation with temperature was given by the data of this paper.

TABLE XXXI.

The Volume of Water at Regular Pressure and Temperature Intervals.

Pressure, kgm./cm.²	Volume.									
	−20°.0.	−15°.0.	−10°.0.	−5°.0.	0°.0.	+5°.0.	+10°.0.	+15°.0.	+20°.0.	+25°.0.
0	....	....	1.0017	1.0006	1.0000	0.9999	1.0001	1.0007	1.0016	1.0028
500	....	....	9800	9783	9776	9782	9791	9800	9812	9825
1000	....	....	9606	9592	9586	9596	9609	9623	9638	9654
1500	....	9401	9413	9404	9407	9420	9435	9451	9467	9483
2000	9233	9240	9248	9257	9265	9281	9298	9315	9332	9349
2500	9083	9092	9102	9115	9131	9148	9166	9185	9203	9222
3000	8957	8966	8978	8991	9009	9026	9044	9063	9081	9100
3500	....	8860	8872	8884	8903	8923	8944	8964	8984	9005
4000	....	8764	8772	8784	8805	8823	8842	8860	8878	8897
4500	....	....	8680	8691	8713	8721	8749	8767	8785	8802
5000	....	....	8593	8604	8626	8643	8661	8678	8696	8714
5500	....	....	....	8531	8548	8565	8582	8599	8616	8633
6000	....	....	....	8464	8480	8496	8513	8529	8545	8561
6500	....	....	....	....	8414	8429	8444	8460	8475	8490
7000	....	....	....	....	8356	8370	8384	8398	8412	8426
7500	....	....	....	....	....	8309	8321	8334	8346	8358
8000	....	....	....	....	....	....	8262	8273	8284	8295
8500	....	....	....	....	....	....	....	8208	8218	8228
9000	....	....	....	....	....	....	....	8149	8157	8165
9500	....	....	....	....	....	....	....	....	8099	8106
10000	....	....	....	....	....	....	....	....	8046	8050

Before discussing the shape of the p-v-t surface as given by the determinations of compressibility, it may be well to review briefly the known behavior of water, especially with regard to the differences it shows when compared with ordinary liquids.

All ordinary liquids show a decreasing compressibility with rising pressure, the compressibility decreasing faster than the volume, and they also show an increasing compressibility with rising temperature. The mathematical equivalent of this last statement is that the thermal dilatation decreases with rising pressure. This normal behavior is exactly as we would expect if we regard the liquid as composed of nuclei of more or less invariable volume, separated by spaces which may be altered in size by pressure and temperature. It is not necessary for a qualitative understanding of the phenomena even to inquire whether these nuclei are subatomic or atomic; that is, whether the major part of the compression is given by the change of volume of the spaces between the atoms or by changes in volume of the atoms themselves.

For water the effects are anomalous. The compressibility decreases with rising pressure, as it does for everything else, but with rising temperature the compressibility at first becomes less, passes through a minimum, and then becomes greater again. This minimum is situated at about 50°. The position of the minimum is nearly independent of pressure but the minimum itself becomes less and less pronounced with rising pressure, and at 3000 kgm. has entirely disappeared. Corresponding to this anomalous behavior, the dilatation shows anomalous behavior with rising pressure, becoming greater with greater pressure at temperatures below 50°. It has been recognized by Amagat as possible, however, that at temperatures below 50° the dilatation would decrease with rising pressure at pressures sufficiently high. In the immediate neighborhood of 0° and atmospheric pressure, there are special anomalies connected with the maximum density point. In particular, the temperature of maximum density, which at atmospheric pressure is at about 4°, is depressed by rising pressure. This depression of the maximum density point is nearly linear with the pressure, and is so rapid that at 300 kgm. it has fallen below the freezing temperature at that pressure. So much has been shown by Amagat,[16] who worked up to 3000 kgm. The results may be briefly summed up in the statement that water, abnormal at low temperatures and pressures, tends to become normal at high temperatures and pressures.

Now consider the information given by the present data, examining first the compressibility data above zero. Of course the rough facts already known appear immediately from an inspection of the figures. The compressibility decreases strikingly with rising pressure and is less at 22° than at 0°. Figure 36 shows the compressibility (= $\left(\frac{\partial v}{\partial p}\right)_\tau$) at 0° and 22°. At 10,000 kgm. it has decreased to 1/4 of its initial

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[16] Amagat, loc. cit.

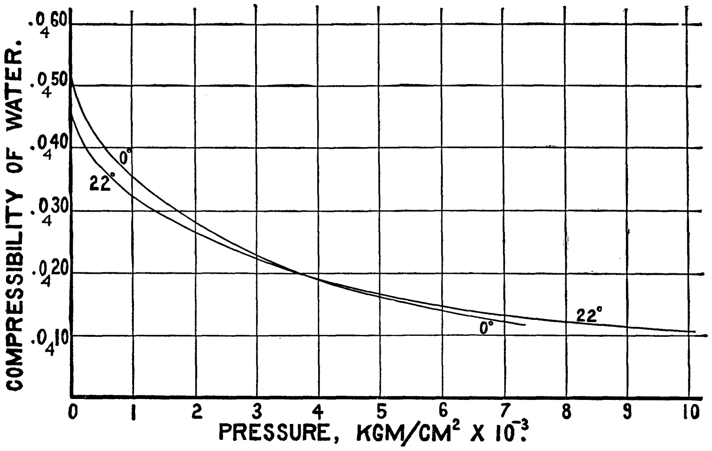

Figure 36. The compressibility $\left(\frac{\partial v}{\partial p}\right)_\tau$ of liquid water as a function of the pressure at 0° and 22°.

value. The figure shows also the crossing of the compressibility curves; at low pressures the compressibility at low temperatures is higher than it is at high temperatures, but with rising pressure the abnormality disappears, and beyond 4000 kgm. the compressibility is higher at the higher temperatures. The variation of thermal expansion between 0° and 22° is shown in Figure 37. This rises to a maximum at nearly 4000 kgm. and then falls again. The rise to the maximum is much more rapid than the fall away from it. This maximum verifies the surmise of Amagat that the dilatation at any temperature would ultimately decrease with rising pressure for pressures sufficiently high. The position of this maximum evidently corresponds to the crossing of the two compressibility curves at 0° and 22°, for we have

$$\frac{\partial}{\partial t}\left(\frac{\partial v}{\partial p}\right) = \frac{\partial}{\partial p}\left(\frac{\partial v}{\partial t}\right) = 0.$$

The usual explanation of the abnormalities shown by water at atmospheric pressure is on the basis of polymerization. The effect of decreasing temperature is to increase the polymerization. For the present purpose we may think of the molecule stable at higher temperatures as a single molecule and that at lower temperatures as a double molecule, although the latter is more probably triple and the former double. The double molecule must furthermore be thought of as occupying more than twice the volume of each of the single molecules of which it is composed. The effect of a decrease of temperature on volume is twofold : a decrease such as takes place in any normal liquid, and an increase due to the clustering of single molecules into double ones. This increase becomes increasingly rapid at low temperatures because of the increasingly rapid polymerization. At 4° it has become sufficiently rapid to neutralize the natural decrease, and at lower temperatures volume increases with falling temperature. The way in which polymerization is affected by pressure can best be discussed after reviewing the data below 0°.

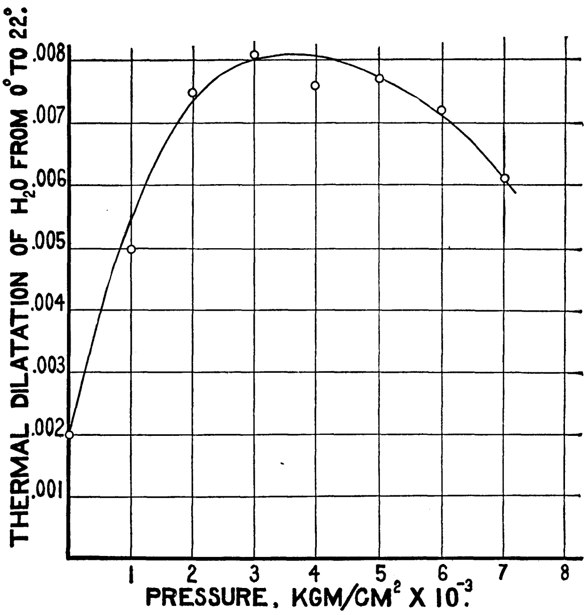

Figure 37. Shows the total change of volume of water between 0° and 22° as a function of the pressure.

The data below 0° show still more strikingly than those above 0°

the abnormality at low pressures followed by normal behavior at high pressures. No previous measurements seem to have been made within this region, although the principal effects are within the reach of previously attainable pressures. At atmospheric pressure the study of water at low temperatures is prevented by the accident of freezing. It will pay us, however, to imagine what would be the relation between temperature and volume on the present theory of polymerization if it were possible to subcool the water indefinitely. At high temperatures we evidently expect the water to behave normally, for its molecules are all single molecules of the same kind, and similarly at very low temperatures, where the molecules are all double molecules, we should expect the behavior to become normal again. The curve connecting volume with temperature for a normal liquid is of the form shown in Figure 38, the dilatation becoming more rapid at high temperatures. These considerations lead us to predict, therefore, a curve of the shape shown in Figure 39 for water. Experimentally it has been found possible to follow this only as far as −10°, not far enough to reach the first point of inflection. The effect of increasing pressure must be to change in some continuous way the curve of Figure 39 into that of Figure 38.

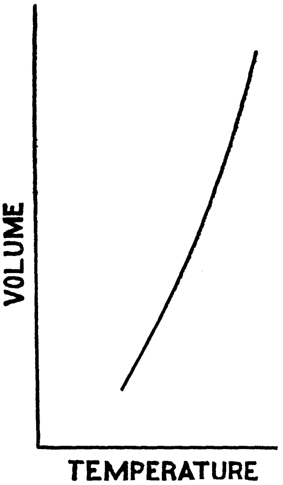

Figure 38. The relation between volume and temperature for a normal liquid.

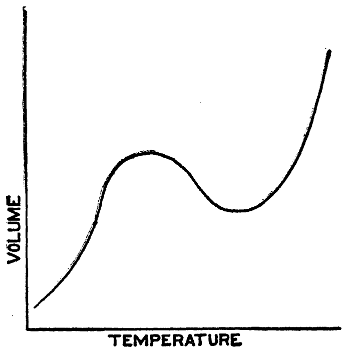

Figure 39. Hypothetical relation between volume and temperature for liquid water if it could be subcooled indefinitely without freezing.

The data indicate very strikingly the way in which the abnormality is effaced. Figure 40 shows this. In this figure the relation between volume and temperature for various constant pressures is plotted directly from the data of Table XXXI. Each separate curve is drawn to scale, but the curves for different pressures have been pushed together, so as to come within the limits of the drawing. The actual separation of the curves is about ten times that shown. The pressure and the value of the volume at 0° are indicated on each curve. The manner of transition from abnormal to normal is shown distinctly, and requires no comment. At 1500 kgm. we actually have realized a curve with both a minimum and maximum, like the conjectural curve at atmospheric pressure. The curves show one thing in connection with the previous experiments, namely, that the depression of the maximum density point with pressure cannot continue linear with pressure much beyond 300 kgm., the limit of the previous experiments, but the temperature of the maximum becomes nearly

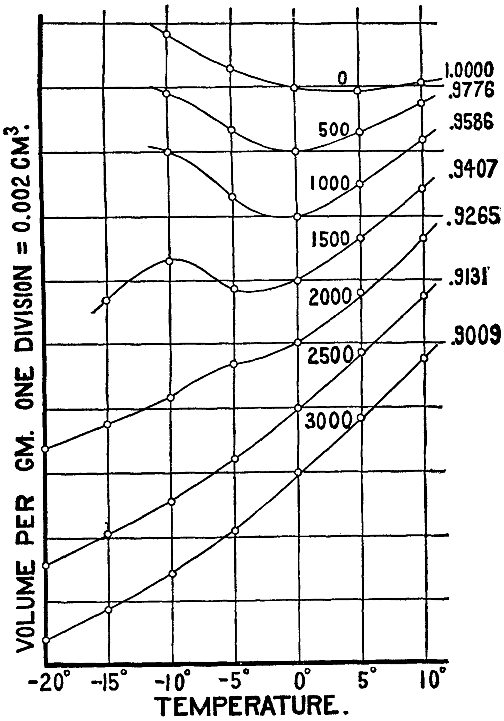

FIGURE 40. Curves showing the relation between volume and temperature of water for various constant pressures. The numbers in the body of the diagram show the constant pressure of each curve; the numbers to the right show the volume at 0° of the liquid at the indicated pressure. If drawn to scale the curves should be separated about ten times as much as shown.

independent of the pressure until the maximum entirely disappears at higher pressures.

Figure 40 shows the results only to 3000 kgm. Up to this point the dilatation at 0° has been increasing with rising pressure. But the fact that the curves of Figure 4 pass through a maximum at about 3200 kgm. indicates a return to normal behavior. From here on the dilatation decreases with rising pressure. The position of this maximum evidently corresponds to the position of the maximum of the dilatation at 3700 kgm. found between 0° and 22°. One would expect some change in the position of the maximum toward lower pressures at lower temperatures, but even if there were none, the agreement is perhaps as good as could be expected when one considers how very small the experimental quantities are which are involved below 0°.

As far as 4000 kgm., the curves of Figure 4 have been in perfect accord with the manner of transition shown in Figure 40. Above 4000, however, if the curves are extrapolated in the direction in which they are heading, there will be new abnormalities. This extension is not actually possible physically, for the same reason that the hypothetical curve connecting volume and temperature at atmospheric pressure was not possible, namely because the water freezes. But the extension may be made, nevertheless, for the purposes of speculation. It is seen that this new abnormality at high pressures and low temperatures consists in a crossing of the lines again, so that at 5000 kgm., for instance, water would expand on passing from –15° to –20°, just as for water at 0° and atmospheric pressure. The explanation suggests itself that this new abnormality is due to the new variety of ice which is about to separate out, either V or VI. At any rate, the idea seems perfectly plausible that each of the forms III, V, and VI is a solid form of water in a different state of polymerization, and that this polymerization should be shown by anomalous effects in the liquid. There certainly seems to be a strong presumption raised for this possibility by the present data. A more accurate experimental investigation would be well worth making, but would require new methods and apparatus.

We now have enough material in the behavior of the curves both above and below 0° to see what the role of pressure in wiping out the abnormalities must be. The one significant fact is that the pressure wipes out the abnormalities where they stand, without any perceptible shifting of their temperatures. Thus above 0°, the temperature of minimum compressibility is very nearly constant at 50°, independent of the pressure. Increasing pressure merely makes this minimum at 50° less and less pronounced until it has entirely disappeared. And below 0° the abnormalities remain confined to the 15° or 20° below 0°, the effect of pressure being merely to smooth out the variation of curvature. Now this is distinctly what one would not expect at first. The usual explanation of the normalizing effect of pressure is to suppose that the amount of polymerization, the cause of the irregularities, is decreased by rising pressure. This is the assumption made by Röntgen [17] and Sutherland.[18] The effect of this evidently would be to displace the region of abnormality from high to low temperatures, which is what we have seen does not happen. The explanation is rather to be found in supposing that the pressure merely reduces the effects of polymerization uniformly at every temperature without necessarily reducing the amount. This means that the difference of volume between the double molecules and the two single molecules becomes rapidly less at higher pressures; in other words, that the double molecules possess an abnormally high compressibility. This seems an entirely plausible hypothesis in view of the abnormally large volume of the double molecules. At high pressures, then, the polymerization, even if it occurs, is unable to produce volume effects, and might as far as we are concerned be entirely neglected. There may be effects on the specific heats, which cannot be detected from the present data. The explanation of the various pressure effects on this basis is simple. The anomalous decrease of compressibility with rising temperature is due to the fact that at the higher temperatures the double molecules with abnormally high compressibility are becoming fewer. When pressure has become so high that there is no longer distinction between the associated and the dissociated molecules, the behavior of the liquid becomes normal. This explanation leaves entirely open the question as to whether pressure actually increases or decreases the amount of polymerization. One would naturally expect an increase. The explanation also leaves open the possibility of the polymerization being to several different groups, more complicated than doublets or triplets. This possibility is suggested by the appearance of the several allotropic forms of ice.

It is to be noticed that in assuming that the molecules are compressible we have not by any means assumed that the actual change of size of the molecules under pressure is the chief factor in the change of volume of the substance as a whole under pressure. In fact it is almost certainly true that the greater part of the total change of volume is due to the closing up of the spaces between the molecules. The substance as a whole may have a greater or less compressibility according as its structure is more or less compressible. Thus liquid water is more compressible than ice I, although it has the smaller volume and is composed of molecules which are themselves less compressible.

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[17] Röntgen, Wied. Ann., **45**, 91–97 (1892).

[18] Sutherland, Phil. Mag., **50**, 460–489 (1900).

TABLE XXXII.

THE VOLUME OF WATER CALCULATED BY TUMLIRZ'S FORMULA COMPARED WITH EXPERIMENTS.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	Volume. cm.^{3}/gm.					
	0°			22°		
	Tumlirz.	Experiment.	Difference.	Tumlirz.	Experiment.	Difference.
0	0.9964	1.0000	−.0036	1.0030	1.0020	+.0010
1000	9560	0.9586	+.0026	0.9629	0.9636	−.0007
2000	9237	9265	+.0028	9318	9340	−.0022
3000	8983	9009	+.0026	9067	9090	−.0023
4000	8778	8805	+.0027	8861	8881	−.0020
5000	8607	8626	+.0019	8690	8703	−.0013
6000	8464	8480	+.0016	8544	8552	−.0008
7000	8341	8356	+.0015	8419	8417	+.0002
8000				8311	8288	+.0023
9000				8216	8161	+.0055
10000				8132	8049	+.0083

With regard to the bearing of these data on the theory of liquids, the theory itself does not seem to be at present far enough advanced so that these data can settle definitely any crucial questions. In fact, there do not seem to be any clear cut questions waiting for settlement. Nearly all the work done so far on liquids has been in modifying van der Waals' equation by making assumptions which seem more or less plausible about the way in which the forces between the molecules, the distances between the molecules, or the energy of the molecules vary with the temperature and pressure, and the chief aim of all this activity seems to have been the production of an equation with as few constants as possible which should accurately represent the behavior of as many liquids as possible under changes of temperature and pressure.

The bearing of these data for water on the theory of liquids as developed in this way may be best shown by testing how well the equations already proposed are applicable by extrapolation over this wider pressure range. For this purpose we may choose the equation given by Tumlirz [19] as perhaps the best. Tumlirz has applied his formula to the data of all the liquids studied by Amagat over a pressure range of 3000 kgm. and a temperature range of 40° or 50°, with really remarkable agreement. Tumlirz's formula has the form

$$(p + P)(v - a) = RT,$$

where a and R are constants for any given substance, and P is a function of the temperature only, to be determined by experiment. The significance of the assumption evidently is that the covolume (proportional to the total volume of the molecules) is independent of pressure and temperature, and that the internal pressure P is not affected by changes of volume at constant temperature. The results calculated by Tumlirz's formula, and the actual experimental results are shown in Table XXXII. The constants used at 0° in the calculation are those given by Tumlirz. At 22°, P was found by interpolation from Tumlirz's values above and below to be 7152. At 0°, the agreement is fairly satisfactory, and the discrepancies are of the same order throughout the entire pressure range. The discrepancies are greatest at the low pressures, corresponding to the abnormal behavior of water here. At 22°, for the lower pressures, the discrepancy is about the same as at 0°, but the most interesting thing about these values at 22° is the very evident failure of the formula at high pressures. The values given by the formula for the compressibility become small too rapidly at the high pressures.

This question as to the behavior of the compressibility at high pressures is the first one that would occur to one as of significance for the theory of liquids at high pressures. That is, does the volume shrink toward a limiting value in the way indicated at low pressures, or is there some other effect introduced by the high pressure? The physical picture of the mechanism of the liquid suggesting this question is that of an assemblage of molecules with intervening spaces. Is the change of volume of the molecules themselves under pressure sufficient to produce an appreciable effect after the intervening spaces have been shut up? The present conception of the atom as a planetary system of electrons would suggest that there are possibilities of enormous change of volume within the atom itself, and that the compression of the atom is going to continue uniform over a relatively enormous pressure and volume range, just as under ordinary circumstances a gas obeys Boyle's law for a relatively very great range of volume and pressure. The fact is that at high pressures the compressibility does remain larger than the formula of Tumlirz demands, whether this is due to a compressible atom or not. The same thing is shown also by the curve of Figure 36 giving compressibility against pressure. The tendency of this curve is to become asymptotic to some value greater than zero, the compressibility changing very slowly at high pressures. At 5000 kgm. the compressibility has dropped to 1/3 of its value at atmospheric pressure, while at 10,000 it is 2/3 of its value at 5000.

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[19] Tumlirz, Sitzber. Wien, Bd. CXVIII, Abt. IIa (Feb., 1909), pp. 1–39.

TABLE XXXIII.

VARIOUS THERMODYNAMIC PROPERTIES OF WATER AT 22°.

Pressure, $\frac{\text{kgm.}}{\text{cm.}^2}$.	$C_p - C_v$. $\frac{\text{gm. cal.}}{\text{gm.}}$.	$\left(\frac{\partial E}{\partial p}\right)_t$ $\frac{\text{gm. cal.}}{\text{gm.}}$.	$\left(\frac{\partial v}{\partial p}\right)_\phi - \left(\frac{\partial v}{\partial p}\right)_\tau$.	$\left(\frac{\partial \tau}{\partial p}\right)_\phi$.
0	0.0079	−0.00159	$0.0_6 37$	0.0016
1000	164	−0.00117	54	19
2000	279	−0.00104	75	23
3000	430	−0.00104	95	26
4000	498	−0.00071	95	26
5000	517	−0.00049	85	24
6000	492	−0.00019	71	22
7000	417	+0.00019	54	19
8000	279	+0.00068	33	15

The compressibility curves for 0° and 22° also indicate one other thing that would be expected, that at sufficiently high pressures the compressibility will become independent of the temperature, or in other words, that the dilatation will approach a value, probably zero, independent of the pressure.

The data obtained for the liquid are sufficient to enable us to calculate certain other quantities of thermodynamic interest. Two of these, the difference of the specific heats and the change of internal energy along an isothermal, may be calculated directly from the given data. Two others, the adiabatic compressibility and the rise of temperature produced by compression, may be computed roughly, merely indicating the direction in which these quantities change under pressure.

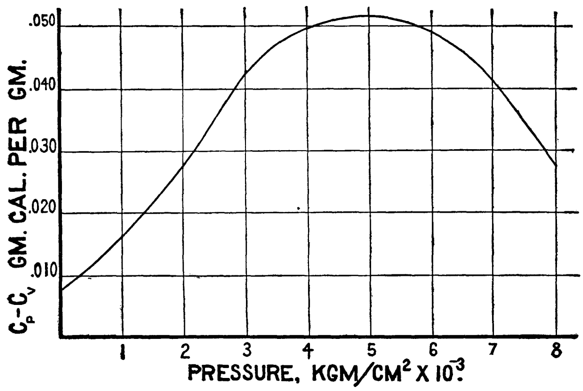

FIGURE 41. The mean difference of the specific heats of the liquid for the temperature range 0°–22°.

The difference of the specific heats is given by the formula

$$C_p - C_p = \frac{-\tau\left(\frac{\partial v}{\partial \tau}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_\tau}.$$

The quantities entering this equation have been determined directly. The computed values for 22° are shown in Table XXXIII., and graphically in Figure 41. The general behavior is a rise to a maximum at 5000 and then a decrease. For a normal liquid $C_p - C_v$ probably decreases continuously with rising pressure. This has been shown to be the case for mercury in the previous paper. The significance of the maximum is, then, merely a repetition of the old story that at high pressure water loses its abnormality and becomes normal. The measurements have not been made to high enough pressures to show the reversal of curvature on the descending branch of the curve, which would show complete attainment of normality. The values of $C_p - C_v$

found here directly differ from those given by the formula of Tumlirz. This formula, used by extrapolation, would demand a continuous increase in the value of $C_p - C_v$ to infinite pressures, suggesting again that there is an effect entering at high pressures not taken account of or foreshadowed by the behavior at lower pressures.

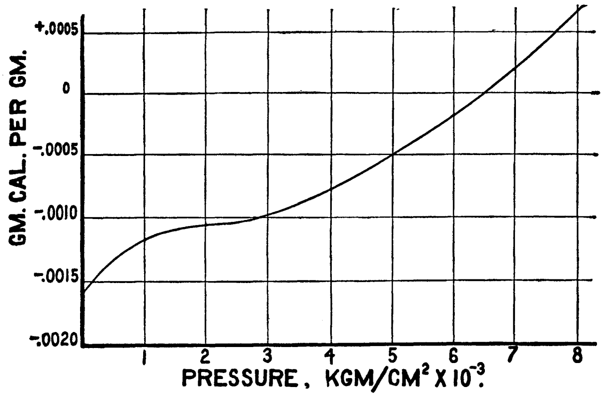

Figure 42. The change of internal energy of the liquid per kgm. rise of pressure along the isothermal at 22°.

The change of internal energy may also be found directly. For this we have the thermodynamic relation

$$\left(\frac{\partial E}{\partial p}\right)_\tau = -\left[\tau\left(\frac{\partial v}{\partial \tau}\right)_p + p\left(\frac{\partial v}{\partial p}\right)_\tau\right].$$

The computed values are shown in Table XXXIII. and Figure 42. Initially the internal energy decreases along an isothermal, but the rate of decrease becomes rapidly less with rising pressure, eventually changing sign, so that at the higher pressures the internal energy increases on an isothermal with increasing pressure. This means that initially the work done in compressing the water is more than lost by dissipation of the high heat of compression, but at higher pressures, the mechanical work per unit rise of pressure has increased so rapidly because of the high pressure that part of the mechanical work expended in compressing the water is retained as increased potential energy after temperature equilibrium has been restored. Except for a region of abnormal curvature, between 2000 and 5000, which is evidently due to the change from an abnormal to a normal liquid, the behavior of $\left(\frac{\partial E}{\partial p}\right)_\tau$ found here is probably typical for any liquid. For mercury, $\left(\frac{\partial E}{\partial p}\right)_\tau$ is initially negative, but it becomes greater algebraically with rising pressure, so that in the mercury paper it was suggested that probably at high enough pressures the energy would increase instead of decrease along an isothermal. Here we have an actual case where the pressure has been pushed far enough to secure this increase. This might have important applications to astrophysics or geophysics, since it shows the possibility of storing up very large amounts of energy in the interior of a star or the earth in virtue of the pressure alone, quite apart from the high temperatures.

Two other quantities of thermodynamic interest, the adiabatic compressibility and the temperature effect of compression, may be roughly approximated to. For these we have the formulae

$$\left(\frac{\partial v}{\partial p}\right)_\phi = \left(\frac{\partial v}{\partial p}\right)_\tau - \frac{\tau}{C_p}\left(\frac{\partial v}{\partial \tau}\right)_p^2,$$

and

$$\left(\frac{\partial \tau}{\partial p}\right)_\phi = \frac{\tau\left(\frac{\partial v}{\partial \tau}\right)_p}{C_p}.$$

Both of these involve the specific heat, which cannot be found from the data obtained, for the specific heat involves the temperature derivative of the dilatation by the well-known relation

$$\left(\frac{\partial C_p}{\partial p}\right)_\tau = -\tau\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p.$$

Measurements of the compressibility at a number of temperatures would be necessary to obtain this. At high pressures, however, $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ becomes less very rapidly. Amagat's data for water show that already at 3000 kgm. and for a temperature range at least from 0° to 30° $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ has vanished within the limits of accuracy. We may assume, then, that at high pressure C_p shows a very slow change. For the rough approximation given here, C_p was taken as constant at 0.9. Tumlirz found C_p at 2000 to be 0.86, but, as already remarked, his value is probably too low. The merely suggestive values for $\left(\frac{\partial v}{\partial p}\right)_\phi - \left(\frac{\partial v}{\partial p}\right)_\tau$ and $\left(\frac{\partial \tau}{\partial p}\right)_\phi$ calculated in this way are shown in Table

XXXIII. The difference between adiabatic and isothermal compressibility increases to a maximum and then decreases. The rise of temperature produced by the application of 1 kgm. pressure also increases and then decreases again. The normal behavior of both these quantities, as shown by mercury, is a continuous decrease, so that here again, we have an effect of the transition from abnormal to normal.

The quantities involved in the change of state from one form to another are shown collectively in the folder at the end, where the equilibrium curves, the change of volume curves, and the latent heat curves are plotted on the same scale for all the modifications. The fundamental question as to the change of state liquid-solid may be stated much more definitely than any fundamental question for the theory of liquids. This fundamental question is as to the ultimate behavior of the liquid-solid curve. Does it end abruptly, indicating a critical point for the transition solid-liquid as many have maintained, or does it rise to a maximum and then descend, as Tammann has claimed in combating the idea of a critical point, or does it merely continue rising indefinitely to infinite pressures and temperatures? Evidently none of these things have happened within the domain of the present diagram for water, nor have they happened in the low range up to 3000 or 4000 used before for any other liquid. The only hold we get on this question is by an extrapolation. In this we are very greatly helped by the behavior of the latent heat and the change of volume, for evidently an extrapolation of the equilibrium curve alone is absolutely incompetent to decide whether it is going to stop abruptly or not. But if this curve has an end or a maximum, then the latent heat and the change of volume must behave in a definite manner with respect to each other. At a critical point, the latent heat and the change of volume must vanish together, while at a maximum, the change of volume becomes zero, the latent heat remaining finite.

Tammann's argument for the probable existence of a maximum comes from observing the general trend of the latent heat and the change of volume on the equilibrium curve. Tammann could not make any very accurate measurements of the change of volume, but they were accurate enough to show that for the substances tried up to 2000 or 3000 kgm. the change of volume becomes less at high pressure, but the latent heat remains nearly constant. The change of volume is approximately linear with temperature on the equilibrium line. Whence by an extrapolation, Tammann concluded that the change of volume would pass through zero before the latent heat, and that therefore the equilibrium curve has a maximum. He has calculated the probable position of this maximum for a number of substances, assuming the melting curve to be a parabola, but this extrapolation is open to very great question. He himself remarks that at high pressures the equilibrium curves tend to show less curvature than one would expect from their behavior at low pressures.

The idea of a maximum seems opposed to our common-sense feeling of what to expect. If there is a maximum, it is possible by taking the substance through an isothermal cycle from the domain of the liquid into that of the solid and back into that of the liquid again to find a necessary connection between the compressibility of liquid and solid over a wide pressure range. This is unexpected in view of our present experience that there is no necessary connection between the properties of liquid and of solid. It is to be noticed that the nearest approach to a maximum found here, on the II–L curve, was neatly avoided by the appearance of another form of ice.

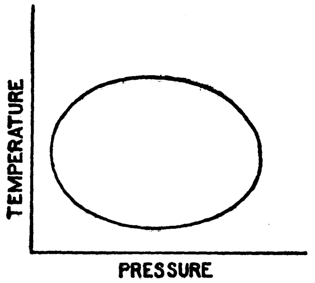

Figure 43. Tammann's complete equilibrium curve between liquid and crystal. The crystal is stable only within the closed region.

Proceeding from the probable existence of a maximum, Tammann has developed his well-known theory of the nature of the complete equilibrium curve between liquid and solid. The ideal curve (Figure 43) according to this theory is a closed curve, the crystalline solid having existence only in the interior of the curve. The complete curve may not be realizable for all substances, since part of the curve may fall at negative pressures or at temperatures below the absolute zero. As a matter of fact, only the two upper quadrants have been realized for known substances, and even then, no substance has been found in both the two upper quadrants. The upper left-hand quadrant is that for normal substances, while the upper right-hand quadrant shows the behavior of water and ice I.

We turn now to the evidence on these points afforded by the present work on water. First for the equilibrium curves alone. These all show curvature in the direction demanded by Tammann's complete diagram, on the I–L curve the fall of temperature becoming more rapid at higher pressures, and on the other curves the rise of temperature becoming less rapid with rising pressure. Except on the I–L curve, this behavior is just exactly what one would expect on nearly any conceivable theory, the effect of temperature becoming less at higher pressures. This is the behavior also on the liquid-vapor curve, which ends in a critical point. From the point of view of Tammann's theory, it is unfortunate that the form I gives place to III at higher pressures, for in the ideal diagram the behavior of I is the normal behavior at high pressure and that of III at low pressures, while here we have a form which should be adapted for the high pressures giving place at high pressure to one apparently appropriate to low pressures.

The change of volume curves next concern us. These also all show the general behavior demanded by Tammann's theory, the change of volume solid-liquid becoming algebraically less at high pressures. On the I–L curve this means that the change becomes numerically greater. The approximate reason of this has already appeared from the discussion of the compressibility of the solid to be merely that the solid is more incompressible than the liquid, whether it has the greater or smaller volume. The curvature of these change of volume curves is also everywhere, except for the curve VI–L, such as to suggest that the change of volume becomes zero at some finite temperature not very far removed from the temperatures actually reached.

The latent heat curves also bear out Tammann's point of view, for they all rise at the higher temperatures on the equilibrium curves. The direction of curvature of these latent heat curves appears to be governed by no such general rule as the change of volume curves, since the curve may be either concave or convex toward the temperature axis.

So far, for the forms of ice I, III, and V, which are stable at low pressures, everything seems as indicated by Tammann's theory. It should be remarked that the pressure range of existence of these forms is twice that reached before. It is on the VI–L curve, however, which reaches to much higher pressures, that we find the significant suggestion as to what to expect at still higher pressures. This suggestion comes from the change of volume curve, which shows a pronounced point of inflection in the neighborhood of 30°.[20] Below 30°, the curvature is like that for the other modifications at low pressures, indicating the vanishing of the change of volume at perhaps 50° or 60°, but beyond 30° the change of volume decreases less and less rapidly with rising temperature, with the possibility of becoming asymptotic.

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[20] With regard to the effect of probable experimental error at the high pressure it is to be said that the effect of this would be to make the inflection shown in the diagram appear less pronounced than it really is. The change of volume at high pressures is too low if anything, because in making the correction for the change in the bore of the cylinder under pressure it was assumed that the increase of bore is linear with pressure, whereas, if anything, it increases more rapidly at high pressures.

That is, at the high pressures there is no indication that the change of volume will ever become zero. This inflection in the volume curve is also mirrored by a corresponding inflection in the latent heat curve, which rises more and more rapidly at the upper end. Also this change of direction of the volume curve occupies the same general locality as the region on the compressibility curves for the liquid where the compressibility ceases to decrease as fast as one would expect from the behavior at low pressures. This behavior of the volume curve, together with that of the latent heat curve, shows in the first place that the latent heat and the change of volume do not vanish together, so that there can be no critical point, and in the second place, that the change of volume apparently will not vanish at any finite temperature, so that we will not have a maximum as supposed by Tammann, but the curve will rise instead to infinite pressures and temperatures.

Recently J. J. van Laar[21] has been developing a theory of the solid state which is more far reaching than that of Tammann, in that it attempts to show the actual mechanism which makes a liquid pass to the solid. This theory explains the solid state by the association of the simple molecules to molecular complexes. For the sake of simplicity, the theory has been developed for the case where the complexes are double molecules, although this restriction is not necessary. Given, then, a liquid in which both single and double molecules may exist, van Laar has found, by writing down the thermodynamic potential of the two kinds of molecules, how the dissociation of the double molecules into single molecules varies with pressure, volume, and temperature. Accompanying the dissociation is a change of volume, for the volume of the double molecule is not in general twice that of the two single molecules from which it comes. This change of volume, due to dissociation, is found to so modify van der Waals' equation, which is still supposed to hold for either kind of molecule separately, that an isotherm now has two maxima and two minima, instead of the single maximum and minimum of van der Waals' original equation. This evidently means the existence of a new phase, the solid, the equilibrium conditions of which are determined in the same way as the equilibrium conditions liquid-gas of the ordinary equation, by applying the condition that the work done in a reversible isothermal cycle is zero.

By detailed numerical computation, van Laar has shown how on this theory the equilibrium pressure solid-liquid changes with increasing temperature. The results are similar to those of Tammann in that a maximum melting temperature and a maximum melting pressure are both predicted. That is, in Figure 43, van Laar has the same maximum and the same right-hand vertical tangent as Tammann, but the results differ from Tammann's in that the minimum and the left-hand vertical tangent cannot exist, or at any rate if they do, they must always lie at temperatures below the absolute zero and at negative pressures.

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[21] van Laar, Proc. Amster., **11**, 765–780 (1909); **12**, 120–132, 133–141 (1909); **13**, 454–475, 636–649 (1910).

These results of van Laar were obtained with the specific assumption that the actual volume of the molecules, and so the change of volume when a double molecule passes into two single molecules, is independent of temperature and pressure. This is almost certainly not the case. The value of the compressibility of water at high pressures, the way in which the abnormalities are smoothed out in the neighborhood of 0°, and the point of inflection in the ΔV curve for VI above 0°, all suggest most strongly that the assumption is not true, and furthermore that it is not approximately enough true to enable even the general character of the melting curve to be predicted at high pressures.

The conclusion of the whole matter seems to be that at high pressures, over 10,000 kgm. for water, we have a new effect appearing, probably connected with the compressibility of the atoms. This means that at high pressures the compressibility of the liquid and solid are going to become more and more nearly equal, which will have as a consequence that the equilibrium curve will continue rising indefinitely.

Besides the data just discussed for the liquid-solid curves, we have the corresponding data for the solid-solid curves. There is no theory at present of the equilibrium solid-solid, and the data here only bear out a remark of Roozeboom [22] that different allotropic solids would be expected to show every conceivable relation to each other. Two triple points between three solid phases had been found, I–II–III, and II–III–V. The first of these is of a type already known, but the second is of a type of which, according to Roozeboom, no examples have yet been discovered. This is Roozeboom's sixth type.[23] The equilibrium lines are for the most part straight, but this merely indicates that the compressibility and thermal dilatation of the solids are nearly constant over the range of temperature and pressure in question, as one might expect. The only curved equilibrium lines are I–III and II–III. In both of these III is involved. But it was to be expected *a priori* that III is a form of ice with more variable properties than the others, because of the close approach of its equilibrium curve with water to a maximum. In general, the internal energy increases on passing from a solid stable at low pressures to the solid stable at higher pressures, but III–II is an exception. The most interesting features found for the equilibrium solid-solid are the probable passing of the I–II curve through the absolute zero, the enormous increase in reaction velocity on approaching a triple point, and the existence in one crystalline form of nuclei about which crystallization to another form may begin.

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[22] Roozeboom, Die Heterogenen Gleichwichte, vol. 1, p. 206. (Vieweg, Braunchweig, 1901).

[23] Roozeboom, loc. cit. p. 202.

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Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.,
October, 1912.

PLATE 1.

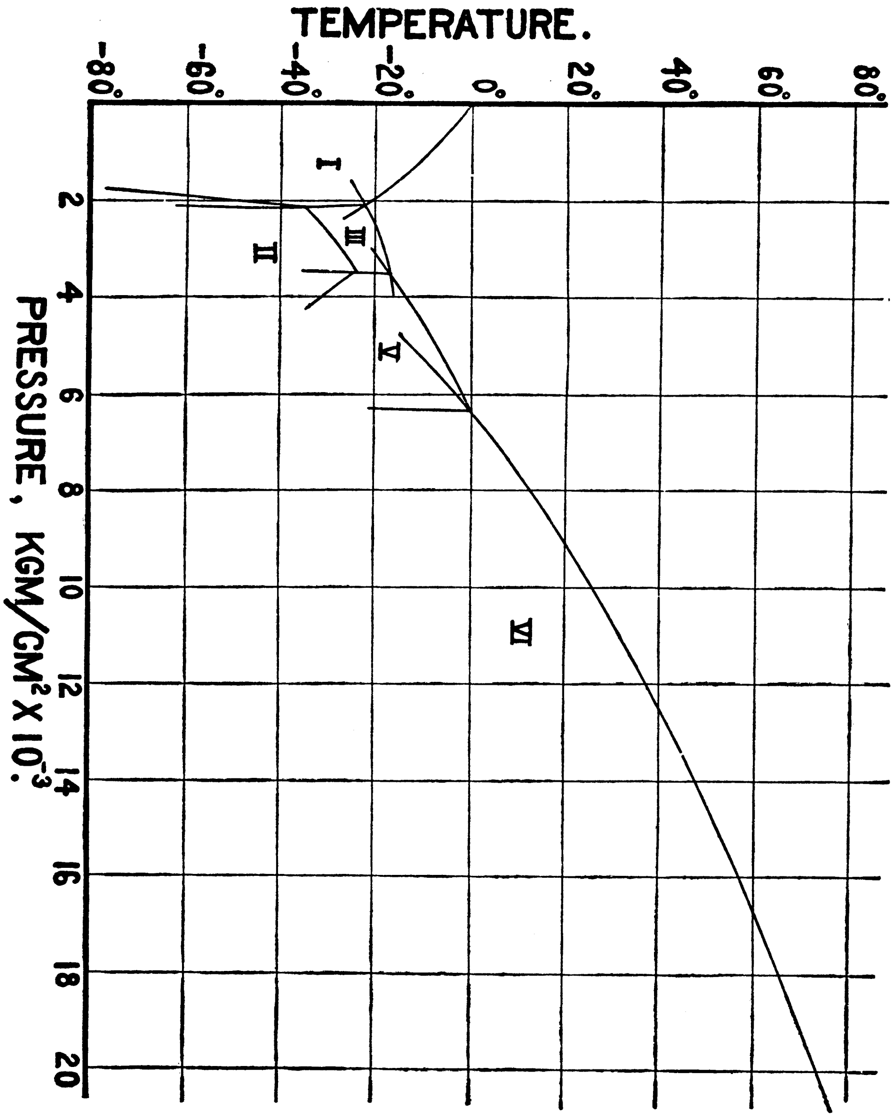
The equilibrium diagram between the liquid and the five solid modifications of water.

PLATE 2.

The change of volume when one modification passes to another under equilibrium conditions.

PLATE 3.

The latent heat when one modification passes to another under equilibrium conditions.


TEMPERATURE.
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
PRESSURE, KGM/GM² X 10⁻³.
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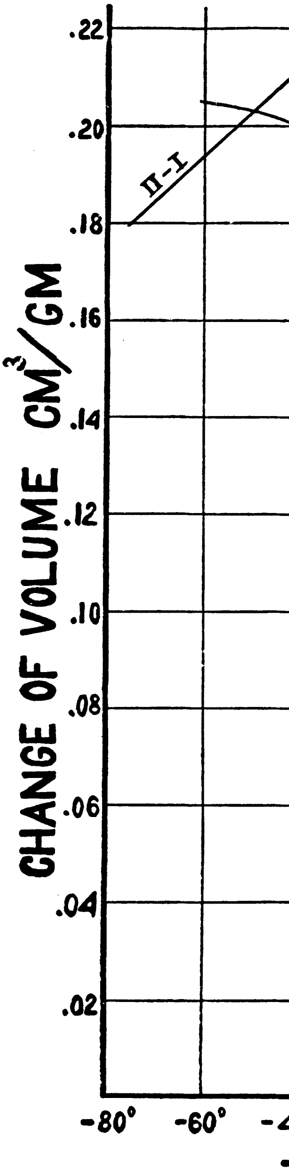
20
I
II
III
V
VI


CHANGE OF VOLUME CM³/GM
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.20
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.14
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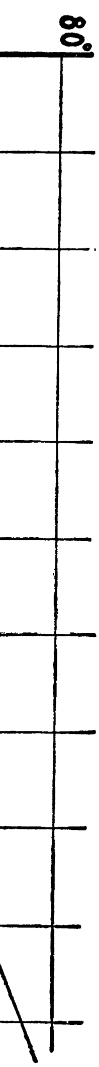
II-I
-80°
-60°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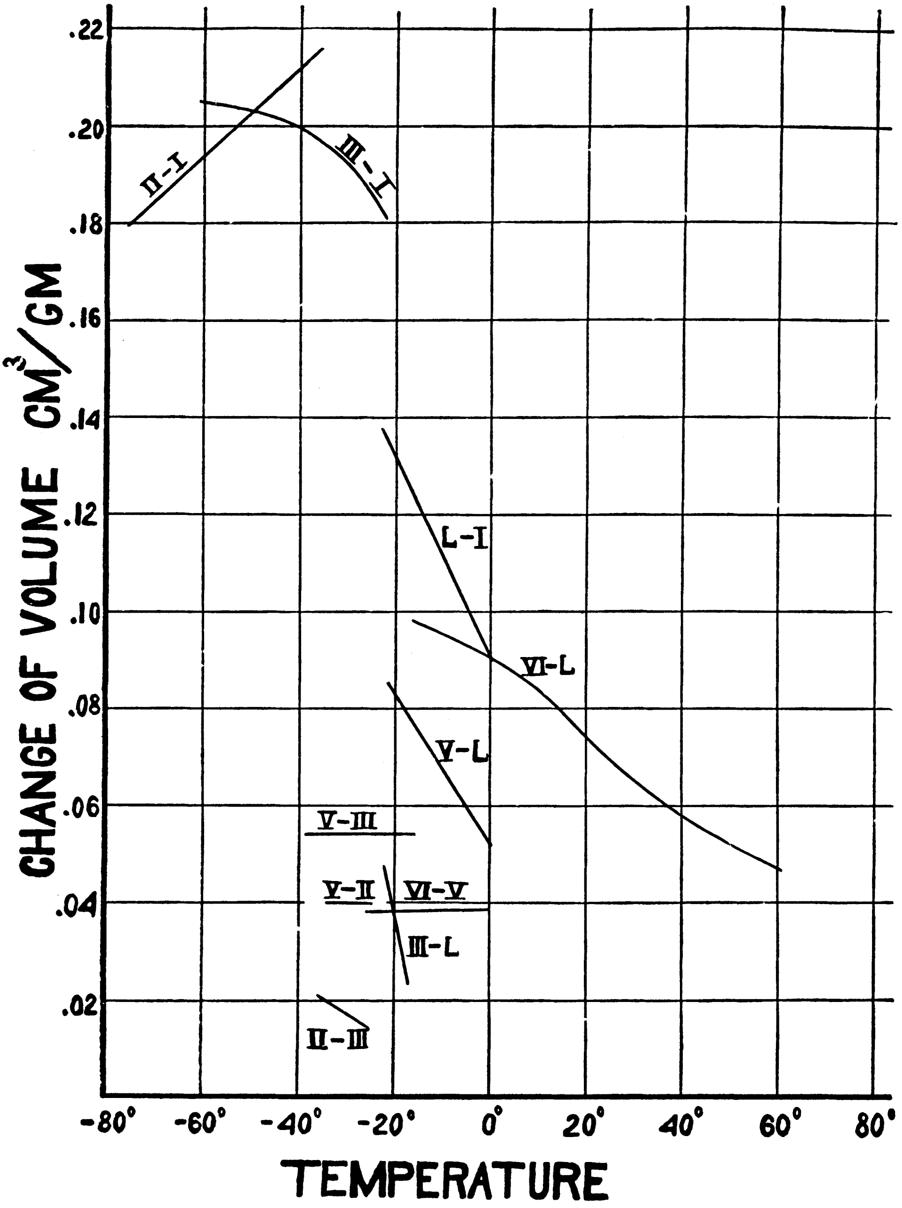
CHANGE OF VOLUME CM^3/GM
.22
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TEMPERATURE
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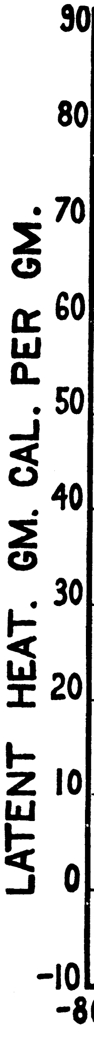
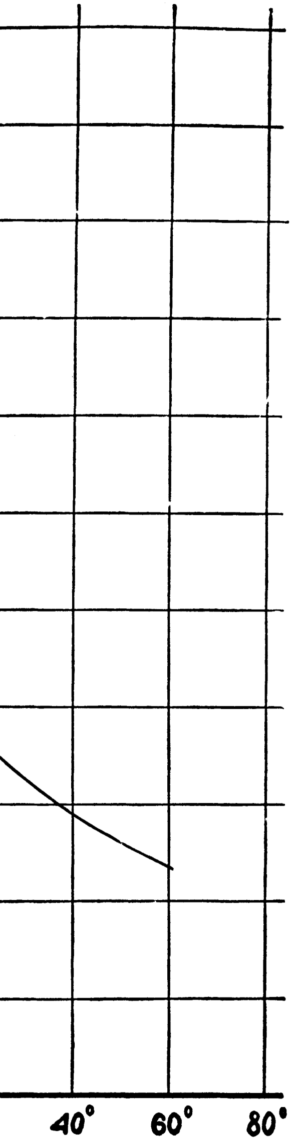
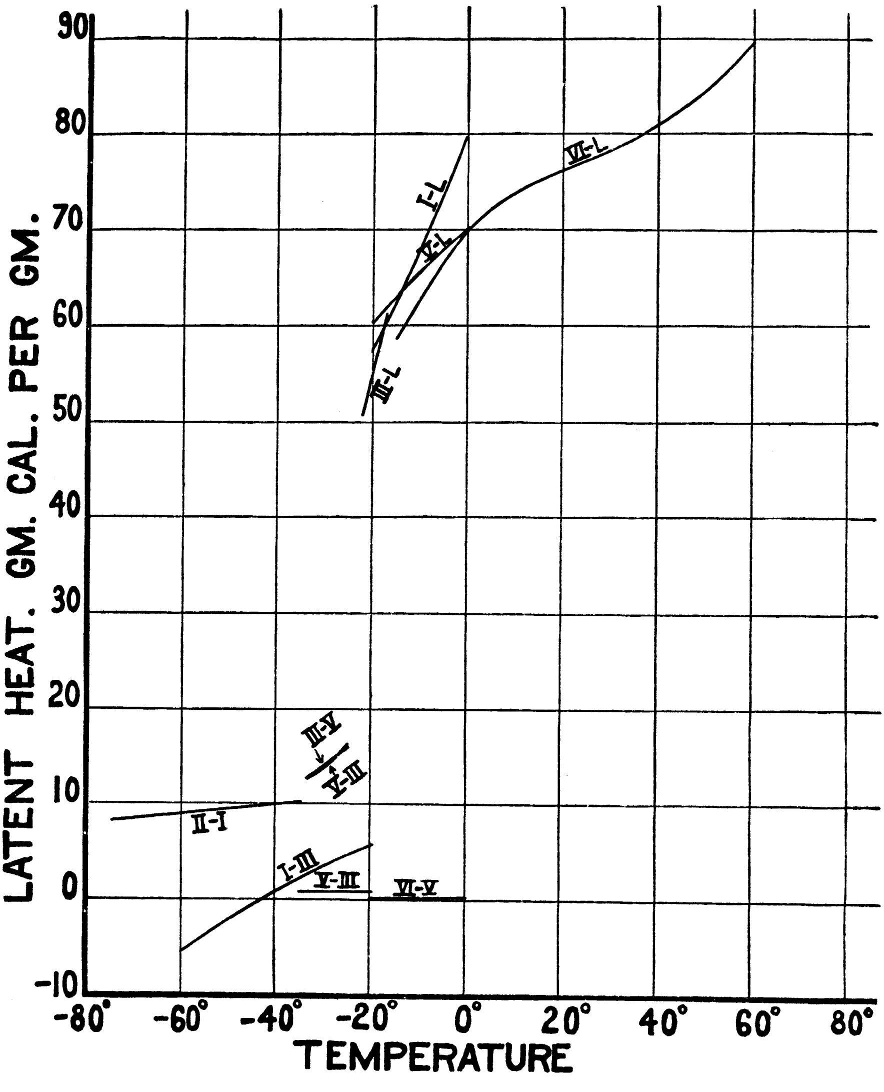
II-III


LATENT HEAT. GM. CAL. PER GM.
90
80
70
60
50
40
30
20
10
0
-10


40°
60°
80°


LATENT HEAT. GM. CAL. PER GM.
90
80
70
60
50
40
30
20
10
0
-10
-80°
-60°
-40°
-20°
0°
20°
40°
60°
80°
TEMPERATURE
VI-L
I-L
V-L
III-L
III-V
V-III
II-I
I-III
V-III
VI-V